5. SOURCES AND EMISSIONS OF ATMOSPHERIC PARTICLES

5.1   INTRODUCTION

Unlike gaseous criteria pollutants (SO_2, NO_2, CO, O_3), which are well defined chemical entities, atmospheric particles comprise a complex mixture of chemical constituents. Because of this fact, sources of each constituent of the atmospheric aerosol must be considered in turn. Since particulate matter (PM) is composed of both primary and secondary constituents, emissions of both the primary components and the gaseous precursors must be considered. The chemical composition of ambient aerosols was treated in general terms in Chapter 3. Information on ambient concentrations of particles of various sizes (PM_{10}, $PM_{2.5}$) and their chemical composition, based on specific field studies, is presented in Chapter 6.

Tables 5-1A and 5-1B summarize anthropogenic and natural sources for the major primary and secondary aerosol constituents of fine and coarse particles. Anthropogenic sources can be further divided into stationary and mobile sources. Stationary sources include fuel combustion for electrical utilities and industrial processes; construction and demolition; metals, minerals, petrochemicals and wood products processing; mills and elevators used in agriculture; erosion from tilled lands; waste disposal and recycling; and fugitive dust from paved and unpaved roads. Mobile, or transportation related, sources include direct emissions of primary PM and secondary PM precursors from highway and off-highway vehicles and nonroad sources. Also shown are sources for precursor gases whose oxidation forms secondary particulate matter. In general, the nature of sources of particulate matter shown in Table 5-1A is very different from that for particulate matter shown in Table 5-1B. A large fraction of the mass in the fine size fraction is derived from material that has been volatilized in combustion chambers and then recondensed to form primary fine PM, or has been formed in the atmosphere from precursor gases as secondary PM. Since precursor gases and fine particulate matter are capable of travelling great distances, it is difficult to identify individual sources of constituents shown in Table 5-1A. The PM constituents shown in Table 5-1B

TABLE 5-1A. CONSTITUENTS OF ATMOSPHERIC FINE PARTICLES (<2.5 μm) AND THEIR MAJOR SOURCES

Aerosol species	Sources			
	Primary		Secondary	
	Natural	Anthropogenic	Natural	Anthropogenic
$SO_4^=$	Sea spray	Fossil fuel combustion	Oxidation of reduced sulfur gases emitted by the oceans and wetlands; and SO_2 and H_2S emitted by volcanism and forest fires	Oxidation of SO_2 emitted from fossil fuel combustion
NO_3^-	—	Motor vehicle exhaust	Oxidation of NO_x produced by soils, forest fires, and lighting	Oxidation of NO_x emitted from fossil fuel combustion; and in motor vehicle exhaust
Minerals	Erosion, re-entrainment	Fugitive dust; paved, unpaved roads; agriculture and forestry	—	—
NH_4^+	—	Motor vehicle exhaust	Emissions of NH_3 from wild animals, undisturbed soil	Emissions of NH_3 from animal husbandry, sewage, fertilized land
Organic carbon (OC)	Wild fires	Open burning, wood burning, cooking, motor vehicle exhaust, tire wear	Oxidation of hydrocarbons emitted by vegetation, (terpenes, waxes); wild fires	Oxidation of hydrocarbons emitted by motor vehicles, open burning, wood burning
Elemental carbon	Wild fires	Motor vehicle exhaust, wood burning, cooking	—	—
Metals	Volcanic activity	Fossil fuel combustion, smelting, brake wear	—	—
Bioaerosols	Viruses, bacteria	—	—	—

TABLE 5-1B. CONSTITUENTS OF ATMOSPHERIC COARSE PARTICLES
(>2.5 μm) AND THEIR MAJOR SOURCES

	Sources			
	Primary		Secondary	
Aerosol species	Natural	Anthropogenic	Natural	Anthropogenic
Minerals	Erosion, re-entrainment	Fugitive dust; paved, unpaved road dust, agriculture and forestry	—	—
Metals	Erosion, re-entrainment, organic debris	—	—	—
Miscellaneous ions	Sea spray	Road salting	—	—
Organic carbon	—	Tire and asphalt wear	—	—
Organic debris	Plant, insect fragments	—	—	—
Bioaerosols	Pollen, fungal spores, bacterial agglomerates	—	—	—

have shorter lifetimes in the atmosphere, so their impacts tend to be more localized. Only major sources for each constituent are listed in Tables 5-1A and 5-1B.

Natural sources of primary PM include windblown dust from undisturbed land, sea spray, and plant and insect debris. The oxidation of a fraction of terpenes emitted by vegetation and reduced sulfur species from anaerobic environments leads to secondary PM formation. Ammonium (NH_4^+) ions which are crucial for regulating the pH of particles are derived from emissions of ammonia (NH_3) gas. Source categories for NH_3 have been divided into emissions from undisturbed soils (natural) and emissions which are related to human activities (e.g., fertilized lands, domestic and farm animal waste). It is difficult to describe emissions from biomass burning as either natural or anthropogenic. Clearly, fuel wood burning is an anthropogenic source of PM, whereas wildfires would be a natural source. Forest fires have been included as a natural source, because of the lack of information on the amount of prescribed burning or accidental fires caused by humans.

Similar considerations apply to the biogenic emissions of trace metals which may be remobilized from anthropogenic inputs.

Although a large number of potential source contributions have been listed for particulate matter and gaseous precursors in Tables 5-1A and 5-1B, it should be noted that emissions inventories have been compiled for only a limited number of entries for either aerosol constituents or source categories. The remainder of the chapter includes discussion of the processes responsible for the most important sources of primary and secondary PM in Sections 5.2 and 5.3, respectively, followed by discussion of emissions estimates for the United States in Section 5.4. Applications of emissions inventories and other techniques, such as receptor modeling for inferring sources of ambient particulate matter, are then discussed in Section 5.5.

5.2   SOURCES OF PRIMARY PARTICULATE MATTER

This section discusses processes responsible for the emissions of primary particulate matter. The order of sources roughly follows their estimated relative source strengths for the United States to be presented in Section 5.4. Emissions of mineral particles produced as the result of natural wind erosion and human activities are discussed in 5.2.1. Sources of primary particulate matter produced by fossil fuel combustion and other stationary anthropogenic sources are discussed in 5.2.2, while sources of secondary particulate matter are discussed in section 5.3. Motor vehicle emissions are discussed in 5.2.3. Vegetation burning in woodstoves and forest fires is discussed as a source of particulate matter in 5.2.4. Sea salt aerosol production, the suspension of organic debris, and the production of trace metals by natural processes are discussed in 5.2.5. Data for the chemical composition and particle size distribution for each of these sources of particulate matter are included where available along with information about techniques for measuring source compositions and emissions rates.

5.2.1   Wind Erosion and Fugitive Dust

Windblown dust constitutes a major component of the atmospheric aerosol, especially in arid and semi-arid areas of the world. Windblown dust represents the largest single category

in global emissions inventories, constituting about 50% of the total global source of primary and secondary particulate matter (IPCC, 1995). Since the next major category is sea-salt aerosol production, which is estimated to constitute about 40% of total emissions, it can be seen that about 70% of non-sea-salt aerosol emitted is in the form of mineral dust. If one-half of the dust is assumed to be emitted in the PM_{10} size range, then it can be seen that 54% of non-sea-salt PM_{10} emitted globally is dust, less than about 10% of which originates in the United States.

Many areas of the western United States are classified as arid or semi-arid, potentially leading to a larger contribution of dust to the mass of the ambient aerosol there compared to the eastern United States. Large-scale dust events are generally associated with semi-arid regions where marginal lands are used for agriculture and herding. During times of drought, the denuded and broken soil surface is easily carried away, periodically forming "dust bowl" conditions as in the midwestern U.S. (Prospero, 1995).

Emission rates of mineral aerosols are found to be strongly dependent on meteorological parameters such as wind velocity and precipitation. Wind tunnel experiments (Bagnold, 1941; Chepil, 1945) have shown that the motion of loose particles on the surface is initiated when the surface wind stress (The wind stress acting on the surface is supplied by the downward transport of momentum from the mean winds. In micrometeorological applications, u^*, or the square root of the ratio of the wind stress to the air density is used.) acting on erodible particles exceeds the downward force of gravity and the interparticle cohesion forces acting on the particles. Particle motion occurs when u^* exceeds the threshold friction velocity, u^*_t, which is dependent on particle properties. Values of u^*_t are strongly size dependent, with a minimum for particles having diameters of about 60 μm (Bagnold, 1941). Individual smaller particles are held by cohesive forces and larger particles are constrained by the force of gravity. Measurements of u^*_t are available for a number of different soil types (e.g., Gillette et al., 1980).

Three types of particle motion were characterized in the early wind tunnel experiments: suspension, saltation, and creeping. Suspension refers to the upward transport of dust (d< 60 μm) by turbulent eddies; saltation to the horizontal motion of particles (60 < d < 2000 μm) which can reach heights of up to a meter above the surface before they fall back;

creeping to particles too massive (d > 2000 µm) to be lifted from the surface so they roll along.

Because of strong cohesive forces in soil crusts and rock surfaces, particles are not suspended directly by the transfer of momentum from the wind but by sandblasting and abrasion by saltating particles. The impact of saltating grains then results in the emission of smaller particles (Shao et al., 1993). The flux of saltating particles increases rapidly with wind speed, and varies as $(u^*)^2(u^*-u^*_t)$. The size distribution of the suspended aerosol is then controlled by the aerosol microphysical processes of coagulation and sedimentation.

Non-erodible elements on natural surfaces cut down on the surface area available for erosion, and they take up wind momentum which would otherwise be available for erosion. Soil moisture, salts, and organic matter mainly affect soil cohesion (e.g., Gillette et al., 1982) and thus the size distribution of soil particle aggregates. Chepil (1956), Belly (1964), Bisal and Hsieh (1966), and Svasek and Terwindt (1974) show that substantially greater wind forces are needed when soil surface moisture is increased by less than 1% from its dry state. The moisture content of soils will vary throughout the year depending on the frequency and intensity of precipitation events, irrigation, and the relative humidity and temperature of the surrounding air. Large amounts of rain falling during 1 mo of a year will not be as effective in stabilizing dust as the same amount of rain interspersed at intervals throughout the year.

An operational difficulty arises because u^* is derived from anemometers placed at a height of 5 or 10 m above the surface and requires assumptions about the wind profile down to the surface. The challenge is to derive values for wind stress acting on erodible elements (Alfaro and Gomes, 1995) which are valid for large areas. Alfaro and Gomes (1995) have derived relations between wind velocity measurements made at conventional heights and surface wind stresses using radar imagery to characterize surface roughness. Surface roughness is determined by the presence of vegetation, structures, rocks and boulders, topographic irregularities and surface obstructions. Marticorena and Bergametti (1995) have developed parameterizations including these physical considerations suitable for use in large scale models.

Apart from the large-scale, mean flow small-scale atmospheric vortices are also capable of suspending dust. Dust devils, so-called because of the dust they entrain, may be found in arid areas along roads or where the surface has been disturbed by human activity (Hall,

1981; Snow and McClelland, 1990). Hall (1981) proposed that dust devils could constitute the major source of suspended dust on hot summer days with light winds and convectively unstable conditions, as an example in Pima Co., AZ demonstrates. Hall (1981) estimated that large scale winds could raise 171 kg km^{-2} day^{-1} and motor vehicles could raise 48 kg km^{-2} day^{-1} on an annually averaged basis, while dust devils could raise up to 250 kg km^{-2} day^{-1} of dust (in all size ranges) on hot summer days. Atmospheric vortices are not a source component currently treated in emissions inventories.

Apart from sources within the continental United States, an additional source of windblown dust involves the long-range transport of dust from the Sahara desert westward across the Atlantic Ocean. Individual dust storms have been tracked across the Atlantic, after emerging from the northwest coast of Africa, to the east coast of the United States (Ott et al., 1991). Saharan dust is carried into the Miami area, capable of producing dense hazes during the summer (Prospero et al., 1987). While summertime monthly mean dust concentrations are about 10 μg/m^3 (Prospero et al., 1993), dust events are highly sporadic and of short duration. In a one-year study of Saharan dust deposition in Miami, Prospero et al. (1987) found that 22% of the annual deposition occurred in one day and 68% in rain events that occurred during two dust episodes spread over a total of four days. Gatz (1995) has found evidence suggesting that Saharan dust has reached as far as central Illinois in at least one episode which occurred during the summer of 1979. Up to 20 μg/m^3 of the ambient aerosol may have originated in the Sahara desert and the Sahel during this episode. These dust events are highly sporadic and more work needs to be done to characterize the frequency, magnitude, and variability of these events. Similar dust transport may also occur from the deserts of Asia across the Pacific Ocean (Prospero, 1995), but it is not clear to what extent any of this dust reaches the United States (See Chapter 6 for more information on long distance transport of dust particles into the United States from Africa or Asia.)

The compositions of soils and average crustal material are shown in Table 5-2 (adapted from Warneck, 1988). Two entries are shown as representations of average crustal material. Differences from the mean soil composition shown can result from local geology and climate conditions. Major elements in both soil and crustal profiles are Si, Al, and Fe which are found in the form of various minerals. In addition, organic matter constitutes a few percent,

**TABLE 5-2. AVERAGE ABUNDANCES OF MAJOR
ELEMENTS IN SOIL AND CRUSTAL ROCK**

| | Elemental Abundances (ppmw) | | |
| | Soil | Crustal Rock | |
Element	(a)	(b)	(c)
Si	330,000	277,200	311,000
Al	71,300	81,300	77,400
Fe	38,000	50,000	34,300
Ca	13,700	36,300	25,700
Mg	6,300	20,900	33,000
Na	6,300	28,300	31,900
K	13,600	25,900	29,500
Ti	4,600	4,400	4,400
Mn	850	950	670
Cr	200	100	48
V	100	135	98
Co	8	25	12

Source: (a) Vinogradov (1959); (b) Mason (1966); (c) Turekian (1971), Model A; as quoted in Warneck (1988).

on average, of soils. In general, the soil profile is similar to the crustal profiles, except for the depletion of soluble elements such as Ca, Mg, and Na.

Because of the enormous difficulties encountered in developing theoretical estimates of windblown dust emissions, most current estimates rely on the results of empirical studies. These studies typically involve the placement of wind tunnels over natural surfaces and then measuring emission rates and size distributions for different wind conditions. The emissions of fugitive dust raised as the result of human activities are also extremely difficult to quantify. Fugitive dust emissions arise from paved and unpaved roads, building construction and demolition, storage piles, and agricultural tilling in addition to wind erosion.

Figure 5-1 shows examples of size distributions in dust from paved and unpaved roads, agricultural soil, sand and gravel, and alkaline lake bed sediments which were measured in a
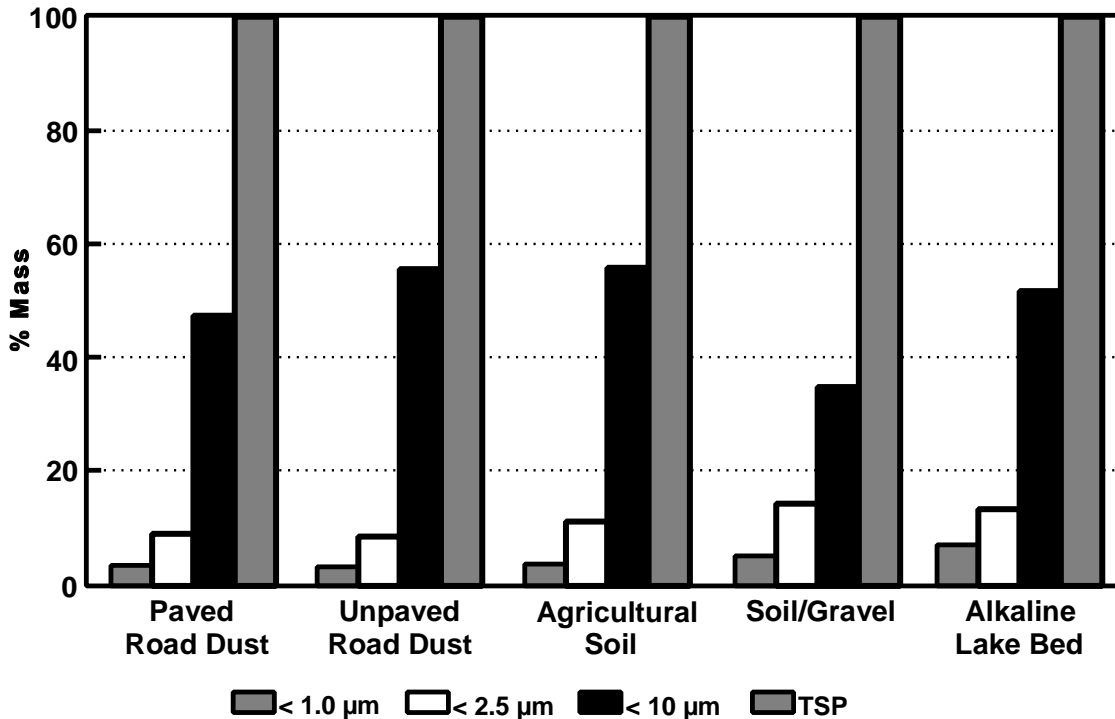
Figure 5-1. **Size distribution of particles generated in a laboratory resuspension chamber.**

Source: Chow et al. (1994).

laboratory resuspension chamber as part of a study in California (Chow et al., 1994). This figure shows substantial variation in particle size among some of these fugitive dust sources. The $PM_{1.0}$ abundance (6.9%) in the alkaline lake bed dust is twice its abundance in paved and unpaved road dust. Approximately 10% of TSP is in the $PM_{2.5}$ fraction and approximately 50% of TSP is in the PM_{10} fraction. The sand/gravel dust sample shows that 65% of the mass is in particles larger than the PM_{10} fraction. The $PM_{2.5}$ fraction of TSP is approximately 30% to 40% higher in alkaline lake beds and sand/gravel than in the other soil types. The tests were performed after seiving and with a short (<1 min) waiting period prior to sampling. It is expected that the fraction of $PM_{1.0}$ and $PM_{2.5}$ would increase with distance from a fugitive dust emitter as the larger particles deposit to the surface at a larger velocity than the smaller particles. Additional data shown in Figure 5-2 (Houck et al., 1989, 1990) were obtained in a study characterizing particle sources in California.
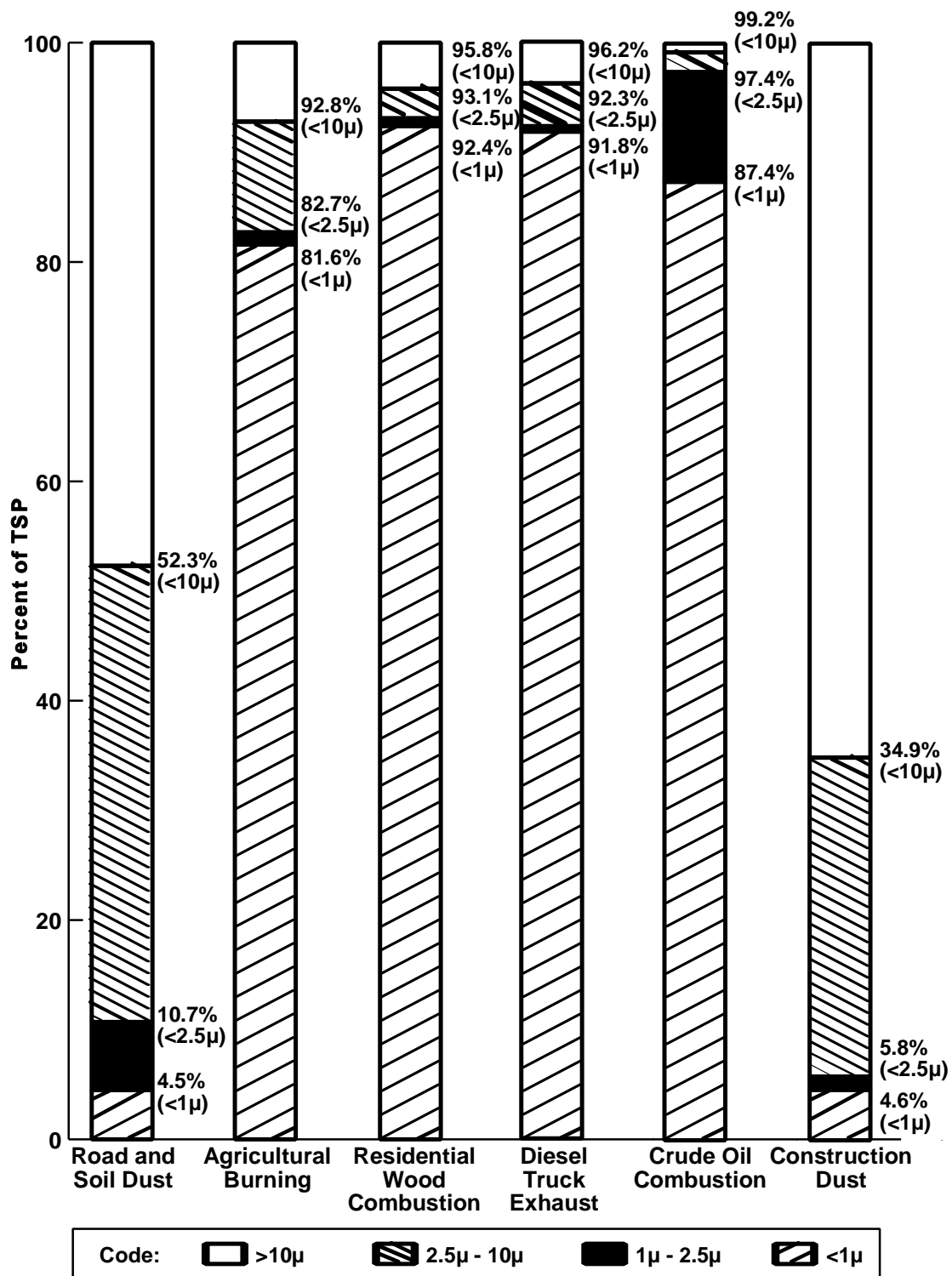
Figure 5-2.   Size distribution of California source emissions, 1986.

Source: Houck et al. (1989, 1990).

Unpaved roads and other unpaved areas with vehicular activity are essentially unlimited reservoirs of dust loading when vehicles are moving. These surfaces are always being disturbed, and wind erosion seldom has an opportunity to increase their surface roughness sufficiently to inhibit particle suspension. The U.S. EPA AP-42 emission factor (U.S. Environmental Protection Agency, 1995a) for unpaved road dust emissions contains variables which account for silt loading, mean vehicle speed, mean vehicle weight, mean number of wheels, and number of days with detectable precipitation, to determine annual PM_{10} dust emissions for each vehicle-kilometer traveled. Dust loadings on a paved road surface build up by being tracked out from unpaved areas such as construction sites, unpaved roads, parking lots, and shoulders; by spills from trucks carrying dirt and other particulate materials; by transport of dirt collected on vehicle undercarriages; by wear of vehicle components such as tires, brakes, clutches, and exhaust system components; by wear of the pavement surface; by deposition of suspended particles from many emissions sources; and by water and wind erosion from adjacent areas. Moisture causes dust to adhere to vehicle surfaces so that it can be carried out of unpaved roads, parking lots, and staging areas. Carryout also occurs when trucks exit heavily watered construction sites. This dust is deposited on paved roadway surfaces as it dries, where it is available for suspension far from its point of origin. Fugitive dust emissions from paved roads are often higher after rainstorms in areas where unpaved accesses are abundant, even though the rain may have flushed existing dust from many of the paved streets.

The size distribution of samples of paved road dust obtained from a source characterization study in California is shown in Figure 5-2. As might be expected, most of the emissions are in the coarse size mode. The chemical composition of paved road dust obtained in Denver, CO, during the winter of 1987-1988 is shown in Figure 5-3. The chemical composition of paved road dust is much like an ambient PM_{10} sample, which consists of a complex mixture of particulate matter from a wide variety of sources. Hopke et al. (1980) found that the inorganic composition of urban roadway dust in samples from Urbana, IL could be described in terms of contributions from natural soil, automobile exhaust, rust, tire wear, and salt. Automobile contributions arose from exhaust emissions enriched in Pb; from rust as Fe; tire wear particles enriched in Zn; brake linings enriched in Cr, Ba, and Mn; and cement particles derived from roadways by abrasion. The complexity
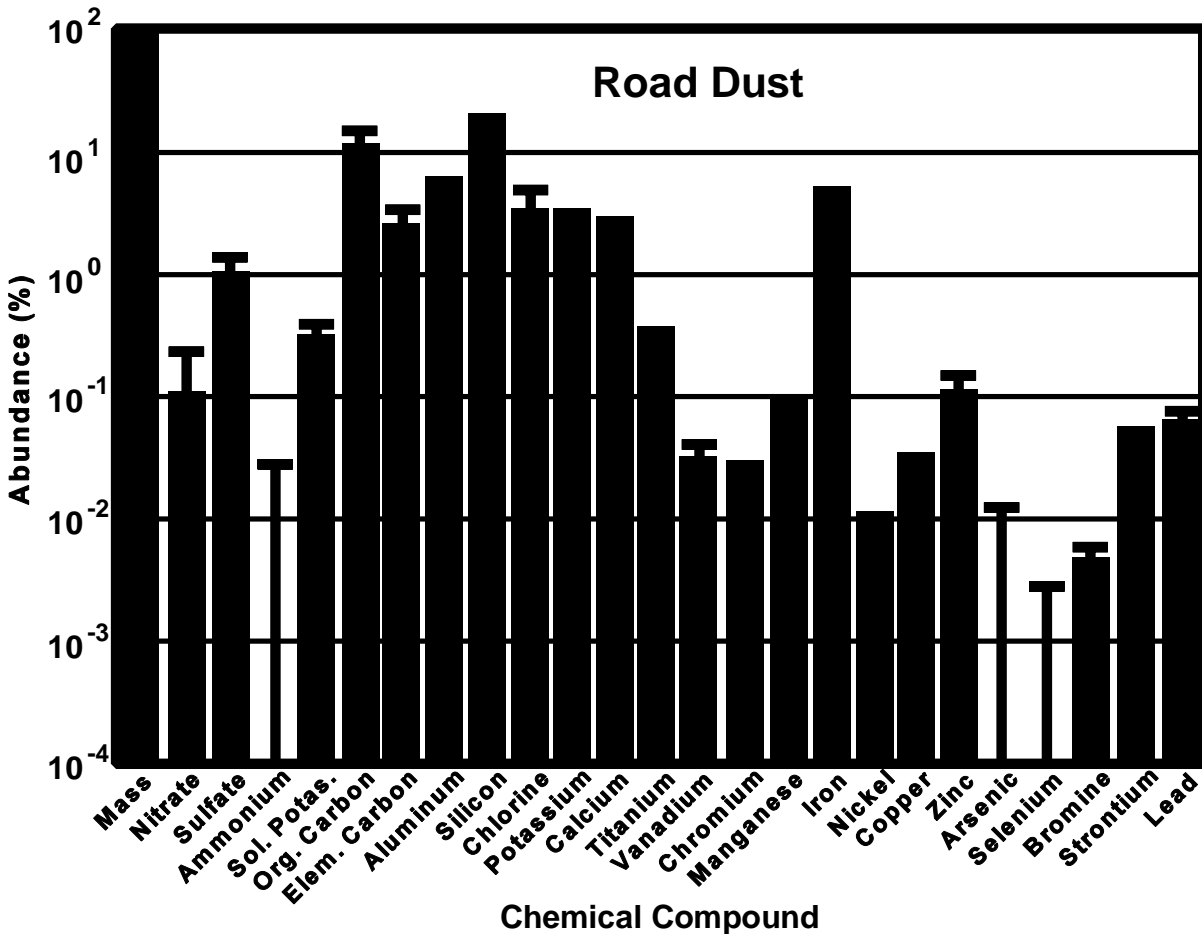
Figure 5-3. Chemical abundances for $PM_{2.5}$ emissions from paved road dust in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

of paved road dust is also evident in the comparison of a paved road dust profile reported by Chow et al. (1991) for Phoenix, AZ, with profiles from other geological sources in the area. Chow et al. (1991) noted that the abundance of organic carbon in the profile was 11±9%, larger and more variable than its abundance in profiles from agricultural land, construction sites, and vacant lots. The presence of particles produced by automotive emissions, tire wear, organic detritus, and engine oils may account for this enrichment for organic carbon. The abundances of Pb and Br in Phoenix paved road dust were more than double the concentrations in the other geological profiles, indicating the presence of tailpipe exhaust from vehicles burning leaded

fuels. The contribution of tire wear could have been from 4 to 45% of that of motor vehicle exhaust, based on the results of Pierson and Brachaczek (1974). Enrichments in species from clutch and brake wear were not detectable in the Phoenix paved road dust profiles. These are often composed of asbestos and/or semi-metal carbon composites. Cooper et al. (1987) examined the elemental composition of semi-metal brake shoes and found abundances of ~45% Fe, ~2% Cu, ~0.5% Sn, ~3% Ba, and ~0.5% Mo. None of these species were found in the Phoenix paved road dust profiles at levels significantly in excess of their abundances in other geological sub-types.

Many fugitive dust sources are episodic rather than continuous emitters. Though windblown dust emissions are low on an annual average, they can be quite large during those few episodes when wind speeds are high. In Coachella Valley, CA, the South Coast Air Quality Management District (1994) calculated 24-h emissions based on a worst windy day. On a day when wind gust speeds exceeded 96 km/h, fugitive dust emissions could account for 20% of the entire annual emissions. Since the rate of dust suspension varies as the cube of the wind speed for large wind speeds, estimates of windblown dust emissions use highest wind speeds quoted in National Weather Service Local Climatological Summaries. Construction activities are also episodic in nature. Reeser et al. (1992) reported that fugitive dust emissions during wintertime in Denver, CO, were 44% higher than those found in the annual inventory using standard emissions inventory methods.

Finally, the spatial disaggregation for fugitive dust emissions is poorer than that for all other source categories. Whereas most mobile sources are confined to established roadways and most area sources are located in populated regions, suspendable dust sources are everywhere. Most fugitive dust emissions are compiled on a county-wide basis and are not allocated to specific fields, streets, unpaved roads, and construction sites possibly contributing to high airborne PM concentrations. Several of these limitations may be impossible to overcome, but many result from old methods being applied to the problem.

The inherent variability of fugitive dust emissions may preclude absolute emissions estimates. Nevertheless, this examination of physical processes shows that better knowledge of the locations of these emissions, the joint frequencies of activities and different meteorological conditions, and more site specific measurements of key parameters could provide much better absolute emissions rates than are now available.

5.2.2   Stationary Sources

The combustion of fossil fuels, such as coal and oil, leads to the formation of both primary and secondary particulate matter. Fossil fuels are mainly composed of a mixture of the remnants of plant matter and surrounding soils which have been processed at elevated temperatures and pressures over periods of up to three hundred million years. The process of coal formation results in a matrix of high molecular weight, highly cross-linked polyaromatic carbocyclic and heterocyclic ring compounds containing C, H, O, N, P, and S, and crustal materials. The hydrogen, nitrogen and phosphorus contents of coal are lower than the original biomass, reflecting losses by microbial utilization and thermal processing. Petroleum consists of long chain straight and branched alkanes with high carbon numbers (i.e., C_{25}-C_{50}), alkenes and aromatic hydrocarbons. The trace element content of these fuels reflects the trace element content of the initial organic matter and soil, subsequent hydrothermal alteration during diagenesis and industrial processing. Because of the inherent variability in each of these factors, the trace element content of fossil fuels is highly variable.

Coal combustion in the high temperature combustion zones of power plants results in the melting and volatilization of refractory crustal components, such as aluminosilicate minerals which condense to form spherical fly ash particles. Fly ash is enriched with metals compared to ordinary crustal material by the condensation of metal vapors. The sulfur content of fossil fuels ranges from fractions of a percent to about 4%. The sulfur in the fuel is released primarily as SO_2 along with smaller amounts of sulfate. Ratios of sulfate S to total S range from about 1% for modern coal fired power plants to several percent in residential, commercial and industrial boilers (Goklany et al., 1984).

The elemental composition of primary particulate matter emitted in the fine fraction from a variety of power plants and industries in the Philadelphia area is shown in Table 5-3 as a representative example of emissions from stationary fossil combustion sources (Olmez et al., 1988). Entries for the coal fired power plant show that Si and Al followed by sulfate are the major primary constituents produced by coal combustion, while fractional abundances of elemental carbon were much lower and organic carbon species were not detected. Sulfate is the major particulate constituent released by the oil fired power plants examined in this study; and, again, elemental and organic carbon are not among the major species emitted. Olmez et al. (1988) also compared their results to a number of similar studies and concluded

**TABLE 5-3. COMPOSITION OF FINE PARTICLES RELEASED BY
VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA**

Species (Units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants						Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
			Eddystone	N	Schuylkill	N								
C-v (%)	ND		2.7 ± 1.2	3	0.75 ± 0.63	4			1.6 ± 1.5	2	ND		0.57 ± 0.26	4
C-e (%)	0.89 ± 0.12	3	7.7 ± 1.5	3	0.22 ± 0.17	4			0.18 ± 0.10	2	0.16 ± 0.05	3	3.5 ± 0.2	4
NH_4 (%)	1.89 ± 0.19	3	3.5 ± 1.6	3	3.7 ± 1.7	4			2.2 ± 0.9	2	0.43 ± 0.22	3	0.36 ± 0.07	4
Na (%)	0.31 ± 0.03	3	3.0 ± 0.8	3	3.3 ± 0.8	3			16.3 ± 0.8	1	0.38 ± 0.05	3	6.6 ± 3.5	3
Al (%)	14 ± 2	3	0.45 ± 0.09	3	0.94 ± 0.08	3			1.74 ± 0.09	1	6.8 ± 1.2	3	0.25 ± 0.10	3
Si (%)	21.8 ± 1.6	9	1.9 ± 0.6	9	2.6 ± 0.4	11			3.1 ± 2.2	2	9.8 ± 20.0	9	1.7 ± 0.3	10
P (%)	0.62 ± 0.10	9	1.5 ± 0.4	9	1.0 ± 0.2	11			0.45 ± 0.27	2	ND		0.63 ± 0.12	10
S (%)	3.4 ± 0.6	9	11 ± 2	9	13 ± 1	11			3 ± 4	2	4.2 ± 12.6	9	2.9 ± 0.8	10
SO_4 (%)	11.9 ± 1.2	3	40 ± 4	3	45 ± 7	4			5.9 ± 2	2	38 ± 4	3	6.8 ± 2.3	4
Cl (%)	0.022 ± 0.11	3	0.019 ± 0.009	2	ND				21 ± 4	1	ND		29 ± 5	3
K (%)	1.20 ± 0.09	9	0.16 ± 0.05	9	0.21 ± 0.03	11			10.9 ± 1.5	2	0.031 ± 0.005	9	7.6 ± 2.3	10
Ca (%)	1.4 ± 0.5	3	3.6 ± 1.0	3	2.3 ± 1.0	3			0.12 ± 0.09	2	0.030 ± 0.004	9	0.23 ± 0.10	10
Sc (ppm)	42 ± 2	3	0.17 ± 0.02	3	0.47 ± 0.02	3			0.092 ± 0.039	1	2.7 ± 0.4	3	0.11 ± 0.02	1
Ti (%)	1.1 ± 0.2	3	0.040 ± 0.044	9	0.12 ± 0.02	11			0.024 ± 0.003	2	0.38 ± 0.1	3	0.030 ± 0.015	10
V (ppm)	550 ± 170	3	11500 ± 3000	3	20000 ± 3000	3			36 ± 7	1	250 ± 70	3	8.6 ± 5.3	2
Cr (ppm)	390 ± 120	3	235 ± 10	3	230 ± 70	3			410 ± 20	1	59 ± 8	3	99 ± 31	3
Mn (ppm)	290 ± 15	3	380 ± 40	3	210 ± 50	3			120 ± 15	1	14 ± 3	3	165 ± 40	3
Fe (%)	7.6 ± 0.4	3	1.6 ± 0.2	3	1.7 ± 0.4	3			0.31 ± 0.02	1	0.20 ± 0.03	9	0.22 ± 0.05	3
Co (ppm)	93 ± 10	3	790 ± 150	3	1100 ± 200	3			13 ± 2	1	15 ± 2	3	3.7 ± 0.8	3
Ni (ppm)	380 ± 50	9	15000 ± 5000	9	19000 ± 2000	11			300 ± 100	2	220 ± 30	9	290 ± 40	10

**TABLE 5-3 (cont'd). COMPOSITION OF FINE PARTICLES RELEASED
BY VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA**

Species (Units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants				Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
			Eddystone	N	Schuylkill	N						
Cu (ppm)	290 ± 20	9	980 ± 320	9	1100 ± 500	11	450 ± 200	2	14 ± 8	9	1300 ± 500	3
Zn (%)	0.041 ± 0.005	3	1.3 ± 0.3	3	0.78 ± 0.30	3	0.079 ± 0.006	1	0.0026 ± 0.0007	3	10.4 ± 0.5	3
As (ppm)	640 ± 80	3	33 ± 6	1	50 ± 16	3	15 ± 6	1	ND		64 ± 34	3
Se (ppm)	250 ± 20	3	26 ± 9	3	23 ± 7	3	66 ± 3	1	15 ± 1	3	42 ± 16	3
Br (ppm)	35 ± 8	3	90 ± 60	9	45 ± 17	11	630 ± 70	2	5.6 ± 1.8	9	2300 ± 800	10
Rb (ppm)	190 ± 80	1	ND		ND		97 ± 38	1	ND		230 ± 50	2
Sr (ppm)	1290 ± 60	9	160 ± 50	9	280 ± 70	11	ND		36 ± 6	9	87 ± 14	10
Zr (ppm)	490 ± 190	9	140 ± 180	9	100 ± 120	11	ND		130 ± 50	2	ND	
Mo (ppm)	170 ± 60	2	930 ± 210	3	1500 ± 300	3	ND		ND		240 ± 130	10
Ag (ppm)	ND		ND		ND		ND		ND		71 ± 15	3
Cd (ppm)	ND		ND		ND		ND		ND		1200 ± 700	3
In (ppm)	0.71 ± 0.04	2	ND		ND		ND		ND		4.9 ± 1.4	3
Sn (ppm)	ND		320 ± 230	9	200 ± 80	11	550 ± 540	2	ND		6700 ± 1900	10
Sb (ppm)	(a)		370 ± 410	3	1020 ± 90	3	6100 ± 300	1	7.7 ± 1.5	3	1300 ± 1000	3
Cs (ppm)	9.2 ± 0.9	2	ND		ND		ND		ND		5.9 ± 3.0	3
Ba (ppm)	ND		1960 ± 100	3	2000 ± 500	3	ND		290 ± 90	2	ND	
La (ppm)	120 ± 10	3	130 ± 30	3	450 ± 30	3	19 ± 2	1	3300 ± 500	3	1.1 ± 0.5	1
Ce (ppm)	180 ± 10	2	89 ± 23	3	360 ± 20	3	ND		2700 ± 400	3	ND	
Nd (ppm)	80 ± 26	3	28 ± 5	2	230 ± 20	3	ND		1800 ± 250	3	ND	
Sm (ppm)	23 ± 2	3	3.7 ± 0.7	3	20.5 ± 1.5	3	ND		170 ± 20	3	ND	

**TABLE 5-3 (cont'd). COMPOSITION OF FINE PARTICLES RELEASED
BY VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA**

Species (Units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants Eddystone	N	Schuylkill	N	Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
Eu (ppm)	5.1 ± 0.5	3	ND		0.65 ± 0.23	3	ND		4.9 ± 0.7	3	ND	
Gd (ppm)	ND		ND		ND		ND		71 ± 10	3	ND	
Tb (ppm)	3.3 ± 0.3	3	ND		0.90 ± 0.29	3	ND		8.9 ± 1.3	3	ND	
Yb (ppm)	10.3 ± 0.5	1	ND		ND		ND		3.7 ± 0.4	3	ND	
Lu (ppm)	ND		ND		ND		ND		0.59 ± 0.17	3	ND	
Hf (ppm)	5.8 ± 0.8	3	0.39 ± 0.07	1	ND		ND		0.99 ± 0.08	3	ND	
Ta (ppm)	ND		ND		ND		ND		0.56 ± 0.10	3	ND	
W (ppm)	20 ± 8	1	60 ± 5	2	ND		ND		ND		ND	
Au (ppm)	ND		0.054 ± 0.017	2	ND		ND		ND		0.56 ± 0.27	3
Pb (%)	0.041 ± 0.004	9	1.8 ± 0.6	9	1.0 ± 0.2	11	0.081 ± 0.014	2	0.0091 ± 0.0021	9	5.8 ± 1.2	10
Th (ppm)	24 ± 2	3	1.9 ± 0.5	2	ND		ND		6.2 ± 0.7	3	ND	
% mass	24 ± 2	6	93.5 ± 2.5	6	96 ± 2	6	81 ± 10	2	97 ± 2	7	89 ± 2	7

N = Number of samples.
ND = Not detected.
The "% mass" entries give the average percentage of the total emitted mass found in the fine fraction.
(a) Omitted because of sample contamination.

Source: Adapted from Olmez et al. (1988).

that their data could have much wider applicability to receptor model studies in other areas with some of the same source types. The high temperature of combustion in power plants results in the almost complete oxidation of the carbon in the fuel to CO_2 and very small amounts of CO. A number of trace elements are greatly enriched over crustal abundances (in different fuels), such as Se in coal and V and Ni in oil. In fact, the higher V content of the fuel oil than in coal could help account for the higher sulfate seen in the profiles from the oil-fired power plant compared to the coal-fired power plant since V is known to catalyze the oxidation of reduced sulfur species. Although Table 5-3 only gives values of the fine particle composition, measurements of coarse particle composition were also reported by Olmez et al. (1988) which were qualitatively similar.

The composition of the organic carbon produced by stationary sources has not been well characterized. Information is available for the composition of polycyclic aromatic hydrocarbons, or PAH's (Daisey et al., 1986), while data for the composition of other classes of organic compounds are sparse. In addition, the phase distribution of a number of PAH's and other organic compounds will depend strongly on ambient atmospheric conditions. It may be expected that the composition of emissions in systems operating at low temperatures (e.g., residential coal combustion) will reflect that of the unburned fuel.

Emissions from stationary sources are determined mainly by stack sampling with a variety of techniques. All these techniques rely on measurements of stack flow rates and concentrations of pollutants to determine emissions. Method 5 (Federal Register, 1977) consists of a sampling train which is commonly used to measure emissions of various trace metals. The method is cumbersome and is limited in the number of species that can be sampled. Based on the realization that direct sampling of hot undiluted stack gases may not yield an accurate representation of the chemical composition and size distribution of particles leaving the stack, dilution sampling has also been used (e.g., Olmez et al., 1988). Condensation, coagulation, and chemical reactions occur as stack gases are cooled and diluted. In dilution sampling, stack gases are diluted with filtered ambient air in an attempt to partially simulate processes occurring in upper portions of the stack and in the plume leaving the stack. Another advantage in the use of dilution systems is that the same sampling substrates and analytical techniques used in ambient sampling can be used. As a result, a wider variety of constituents can be sampled than in conventional direct sampling techniques and biases resulting from the use of separate sampling

systems in source apportionment studies are eliminated. Remote monitoring methods (e.g.,
differential optical absorption spectroscopy) have also been used to determine emissions of
species such as Hg. The size distribution of particles emitted by burning crude oil is shown in
Figure 5-2. As can be seen, almost all of the mass is in the fine fraction.

Apart from emissions in the combustion of fossil fuels, trace elements are emitted as the
result of various industrial processes such as steel and iron manufacturing and non-ferrous metal
production (e.g., for Pb, Cu, Ni, Zn, and Cd) as may be expected, emissions factors for various
trace elements are highly source-specific (Nriagu and Pacyna, 1988). Inspection of Table 5-3
reveals that the emissions from the catalytic cracker and the oil-fired power plant are greatly
enriched in rare-earth elements such as La compared to other sources.

Emissions from municipal waste incinerators are dominated by Cl arising mainly from the
combustion of plastics and metals that form volatile chlorides. The metals can originate from
cans or other metallic objects and some metals such as Zn and Cd are also additives in plastics or
rubber. Many elements such as S, Cl, Zn, Br, Ag, Cd, Sn, In, and Sb are enormously enriched
compared to their crustal abundances. A comparison of the trace elemental composition of
incinerator emissions in Philadelphia, PA (shown in Table 5-3) with the composition of
incinerator emissions in Washington D.C., and Chicago, IL, (Olmez et al., 1988) shows
agreement for most constituents to better than a factor of two. High levels of Hg associated with
emissions from medical waste incinerators from discarded thermometers, mercurials, mercury
batteries, etc., have been declining because of reductions in the use of Hg for medical purposes
(Walker and Cooper, 1992). A sizable fraction of the Hg may be particulate Hg(II) as opposed
to gas phase Hg^0.

5.2.3   Mobile Sources

Particulate matter from motor vehicles originates from tailpipe exhaust and from friction
acting on individual components such as tires and brakes. Both diesel and gasoline fueled
vehicles are sources of primary and secondary particulate matter. The rates of emission and the
composition of particles emitted by motor vehicles have been measured using dynamometers
with samples collected directly in the exhaust of individual vehicles (e.g., Lang et al., 1982) or at
the vents of inspection facilities (e.g., Watson et al., 1994a); or in tunnels and along open
roadways (e.g., Pierson and Brachaczek, 1983; Szkarlat and Japar, 1983). Each approach has its

merits and limitations and each approach is best used to augment the other. The principal components emitted by diesel and gasoline fueled vehicles are organic carbon (OC) and elemental carbon (EC) as shown in Table 5-4. As can be seen, the variability among entries for an individual fuel type is large and overlaps that found between different fuel types. On average, the abundance of elemental carbon is larger than that of organic carbon in the exhaust of diesel vehicles, while organic carbon is the dominant species in the exhaust of gasoline fueled vehicles. There appears to be a tendency for emissions of elemental carbon to increase relative to emissions of organic carbon for gasoline fueled vehicles as simulated driving conditions are changed from a steady 55 km /hr to those in the Federal Test Procedures (FTP's). Also shown are the results of sampling from mixed vehicle types along roadsides and in tunnels.

The results shown in Table 5-4 were obtained during the late 1980's, and, so, the results may not be entirely representative of current vehicles. Examples of data for the trace element composition of motor vehicle emissions obtained in Phoenix, AZ are shown in Table 5-5. SO_2 emissions are also shown in relation to the mass of fine particles emitted. As can be seen, small quantities of soluble ions such as $SO_4^=$ and NH_4^+ are emitted. The ammonium may be emitted as the result of an improperly functioning catalytic converter, or may simply be the result of contamination during sample handling and analysis. Four fractions are given for the organic carbon fraction and three for elemental carbon. These refer to abundances measured at different temperatures in a thermographic analysis. Temperatures for OC1, OC2, OC3, and OC4 are 120 °C, 250 °C, 450 °C, and 550 °C, respectively; and, for EC1, EC2, EC3, they are 550 °C, 700 °C, and 800 °C, respectively, in He/2% O_2. The abundances of trace elements are all quite low, with most being less than 1%. It is not clear what the source of the small amount of Pb seen in the auto exhaust profile is. It is extremely difficult to find suitable tracers for automotive exhaust since Pb has been removed from gasoline. However, it should also be remembered that restrictions in the use of leaded gasoline have resulted in a dramatic lowering of ambient Pb levels. Huang et al. (1994) attempted to identify marker elements in motor vehicle emissions, based on sampling the exhaust of 49 automobiles. They proposed that the combination of Zn, Br, and

**TABLE 5-4. FRACTIONAL ORGANIC AND ELEMENTAL CARBON
ABUNDANCES IN MOTOR VEHICLE EMISSIONS**

Fuel Type	Organic Carbon	Elemental Carbon	N[e]	Sources
Diesel				
Denver, CO[a]	23 ± 8%	74 ± 21%	3	1, 2
Los Angeles, CA[a]	36 ± 3%	52 ± 5%	2	3, 4, 5, 6
Bakersfield, CA[b]	49 ± 13%	43 ± 8%	3	7
Phoenix, AZ[b]	40 ± 7%	33 ± 8%	8	8
Unleaded gasoline				
Denver, CO[a]	76 ± 29%	18 ± 11%	8	1, 2
Los Angeles, CA[c]	93 ± 52%	5 ± 7%	11	3, 4, 5, 6
Los Angeles, CA[a]	49 ± 10%	39 ± %	11	3, 4, 5, 6
Phoenix, AZ[b]	30 ± 12%	14 ± 8%	9	8
Leaded gasoline				
Denver, CO[a]	67 ± 23%	16 ± 7%	3	1, 2
Los Angeles, CA[c]	52 ± 4%	13 ± 1%	3	3, 4, 5, 6
Los Angeles, CA[a]	31 ± 20%	15 ± 2%	3	3, 4, 5, 6
Mixed (tunnel and roadside)				
Denver, CO	50 ± 24%	28 ± 19%		1, 2
Los Angeles, CA[d]	38 ± 6%	38 ± 5%	3	3
Phoenix, AZ	39 ± 19%	36 ± 11%		8

Sources: (1) Watson et al. (1990a), (2) Watson et al. (1990b), (3) Cooper et al. (1987), (4) NEA (1990a),
(5) NEA (1990b), (6) NEA (1990c), and (7) Houck et al. (1989), cited in (8) Watson et al. (1994a).

Notes: (a) Modified Federal Test Procedures followed in dynamometer tests; (b) Roof monitoring at
inspection station; (c) 55 km/hr steady speed in dynamometer tests; (d) Rt. 1 tunnel at LA airport,
(e) N = Number of samples.

Sb could be used for this purpose. However, the relative abundances of these species in
automobile exhaust were shown to be highly variable, implying that other sources of these
elements may limit their usefulness as automotive tracers in some locations. To minimize

TABLE 5-5. PHOENIX PM$_{2.5}$ M0TOR VEHICLE EMISSIONS PROFILES (% MASS)

Chemical Species	Auto	Diesel
NO$_3^-$	3.9 ± 2.9	0.31 ± 0.40
SO$_4^{2-}$	2.3 ± 1.3	2.4 ± 1.0
NH$_4^+$	1.7 ± 1.0	0.87 ± 0.13
OC	30.1 ± 12.3	40.1 ± 6.6
OC1	11.3 ± 3.5	21.0 ± 6.3
OC2	9.2 ± 6.8	9.1 ± 1.9
OC3	4.6 ± 2.2	5.9 ± 1.3
OC4	3.5 ± 1.5	4.0 ± 1.5
EC	13.5 ± 8.0	32.9 ± 8.0
EC1	11.7 ± 7.2	4.4 ± 1.3
EC2	3.1 ± 1.6	27.9 ± 5.6
EC3	0.15 ± 0.30	0.69 ± 0.82
Al	0.41 ± 0.20	0.17 ± 0.12
Si	1.64 ± 0.88	0.46 ± 0.18
P	0.11 ± 0.07	0.06 ± 0.06
S	1.01 ± 0.48	1.24 ± 0.28
Cl	0.34 ± 0.32	0.03 ± 0.06
K	0.25 ± 0.14	0.04 ± 0.03
Ca	0.71 ± 0.41	0.16 ± 0.06
Ti	0.07 ± 0.13	0.00 ± 0.15
Cr	0.02 ± 0.01	0.00 ± 0.01
Mn	0.10 ± 0.04	0.01 ± 0.01
Fe	0.68 ± 0.42	0.16 ± 0.07
Cu	0.07 ± 0.06	0.01 ± 0.01
Zn	0.27 ± 0.22	0.07 ± 0.02
Sb	0.02 ± 0.13	0.01 ± 0.14
Ba	0.06 ± 0.40	0.14 ± 0.47
La	0.15 ± 0.51	0.18 ± 0.59
Pb	0.16 ± 0.07	0.01 ± 0.03
SO$_2$[a]	32.8 ± 13.9	66.9 ± 24.0

Source: Watson et al. (1994a).

Note: Elemental abundances ≤0.01% (V, Co, Ni, Ga, As, Se, Br, Rb, Sr. Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Au, Hg, Tl, U) in XRF analyses excluded; OC = organic carbon; EC = elemental carbon.

[a]Relative to total PM$_{2.5}$.

errors arising from the loss of Br from filters, samples should be analyzed as soon as possible after collection (O'Connor et al., 1977).

The chemical mechanisms responsible for the formation of carbonaceous particles in diesel engines are not well established but are thought to involve the intermediate formation of polycyclic aromatic hydrocarbons, or PAH's (U.S. Environmental Protection Agency, 1993). Elemental carbon particles may be formed by the polymerization of gaseous intermediates adsorbed on a core of refractory material. The particles are in the form of chain or cluster agglomerates at temperatures above 500 °C. At temperatures below 500 °C, high molecular weight organic compounds condense on the carbon chain agglomerates. Roughly 10-40% of particulate emissions from diesels are extractable into organic solvents (National Research Council, 1982). In a typical profile, 50% of the extract is composed of aliphatic hydrocarbons with 14-35 C atoms and alkyl substituted benzenes; 4% are PAH's and heterocycles; and about 6% are PAH oxidation products including a small fraction of nitro-PAH's. The highly polar fraction of the organic emissions has not been as well characterized (Johnson, 1988). Inorganic compounds such as sulfuric acid are also produced in diesel engines (Truex et al., 1980).

Particulate matter is also formed in internal combustion engines as the result of the incomplete combustion of gasoline with contributions from engine oil. The particles consist essentially of a solid carbon core with a coating of organic compounds, sulfate, and trace elements. The composition of PAH's, oxy-PAH's and their alkyl homologues in tailpipe emissions from gasoline fueled vehicles is similar to that produced in diesel engines (Behymer and Hites, 1984). Particles produced by gasoline fueled vehicles range from 0.01 to 0.1 μm in diameter with a peak at around 0.02 μm, while the majority of particles in diesel exhaust range from 0.1 to 1.0 μm with a peak at around 0.15 μm (U.S. Environmental Protection Agency, 1993).

The concentrations of particulate matter and total hydrocarbons in the exhaust of gasoline fueled vehicles were found to be roughly correlated with each other by Hammerle et al. (1992). Emission factors for particulate matter in the exhaust of gasoline fueled vehicles range from 0.011 g/km for light duty vehicles to 0.12 g/km for heavy duty gasoline vehicles, and from 0.23 g/km in the exhaust of diesel passenger vehicles to 1.20 g/km for heavy duty diesel vehicles (Radwan, 1995). These values are based on characteristics of the motor vehicle fleet in 1990.

As mentioned before, the composition of automotive emissions is sampled using individual vehicles on chassis dynamometers or by collecting aerosol samples along roadsides or in tunnels. The control over operating characteristics by using dynamometers allows the development of models which can predict emissions on the basis of variables such as vehicle make and age and driving cycle. The representativeness of dynamometer test data can be questioned if volunteered vehicles, as opposed to randomly selected vehicles, are sampled. In addition, measuring emissions from individual vehicles is also costly and the sample numbers are usually small, as reflected in the small number of samples shown in Table 5-4. Moreover, a number of driving practices are not reflected in the Federal Test Procedures leading to significant underestimates of emissions of CO and hydrocarbons (Calvert et al., 1993). It is still not clear what effects superemitters and off-cycle driving practices have on particle emissions rates. If the relation between particulate matter and hydrocarbon emissions discussed above is representative of the vehicle fleet, the effects could be substantial. Hansen and Rosen (1990) measured the ratio of light-absorbing carbon to CO_2 in the exhausts of 60 gasoline fueled vehicles. They found a factor of 250 difference between the highest and lowest ratios measured. Larger scale studies designed to assess the variability of particulate emissions from motor vehicles are lacking.

Roadside and tunnel measurements sample large numbers of vehicles of different types and have demonstrated their potential for validating the predictions of emissions models. However, the extent to which traffic conditions in the tunnel reflect those in the situation under study must be defined for the results to be considered representative. The same considerations can be extended to dynamometer studies and to open-road studies along road segments. Results from some tunnel studies are of limited usefulness because they have been obtained under highway driving conditions which may not be representative of the conditions found in most urban and suburban areas. Additional uncertainties result from resuspended dust in using tunnel and roadside studies to characterize motor vehicle emissions. However, methods are available for estimating contributions from tire wear (Pierson and Brachaczek, 1974, 1976). Remote measurements of elemental carbon in the exhaust plumes of individual vehicles (Hansen and Rosen, 1990) can overcome many of these difficulties, but the method cannot yet be applied to aerosol constituents other than elemental carbon.

5.2.4   Biomass Burning

In addition to fossil fuels, biomass in the form of wood may be burned in forest fires or as fuel for heating or cooking. At first glance these two broad categories might seem to serve to distinguish between natural and anthropogenic sources. However, many forest fires result from human intervention, either deliberately through prescribed burning in forest management or accidentally through the improper disposal of flammable material or fugitive sparks (e.g., Andreae, 1991). On the other hand, human intervention also suppresses lightning triggered fires. Not enough data is available to assess the effects of humans on forest fires, except for land clearing for agriculture. In contrast to the mobile and stationary sources discussed earlier, emissions from biomass burning in woodstoves and forest fires are strongly seasonal and can be highly episodic within their peak emissions seasons. Burning fuelwood is confined mainly to the winter months and is acknowledged to be a major source of ambient air particulate matter in the northwestern United States during the heating season. Forest fires mainly occur during the driest seasons of the year in different areas of the country and are especially prevalent during prolonged droughts.

An example of the composition of fine particles ($PM_{2.5}$) produced by woodstoves is shown in Figure 5-4. These data were obtained in Denver during the winter of 1987-1988 (Watson and Chow, 1994). As was the case for motor vehicle emissions, organic and elemental carbon are the major components of particulate emissions from wood burning. It should be remembered that the relative amounts shown for organic carbon and elemental carbon will vary with the type of stove, the stage of combustion and the type and condition of the fuelwood. Potassium (K) is by far the major trace element found in woodstove emissions (Watson and Chow, 1994), making it suitable for use as a tracer for vegetation burning (Lewis et al., 1988). Fine particles are dominant in studies of wood burning emissions. For instance, the mass median diameter of wood-smoke particles was found to be about 0.17 μm in a study of the emissions from burning hardwood, softwood and synthetic logs (Dasch, 1982).
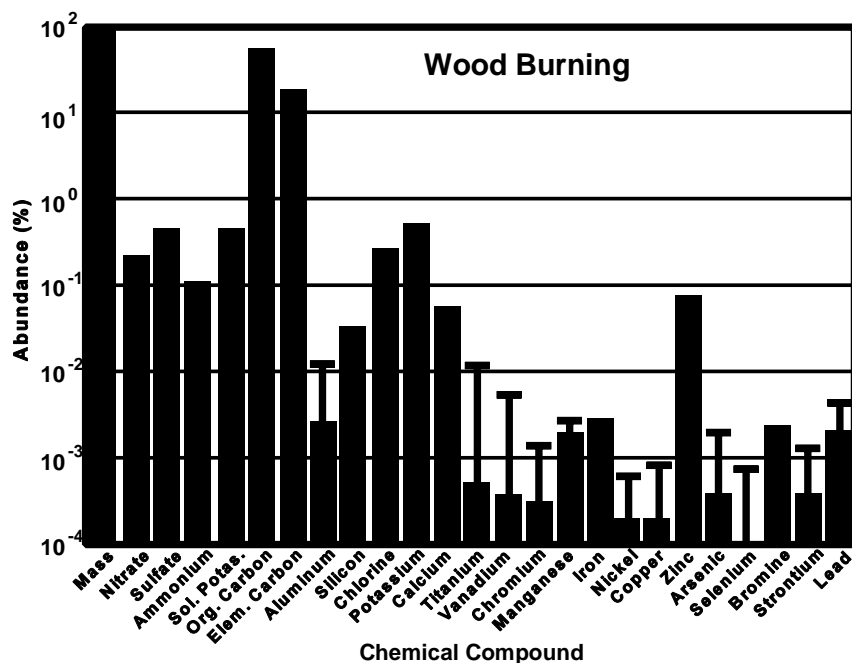
Figure 5-4. **Chemical abundances for PM$_{2.5}$ emissions from wood burning in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.**

Source: Watson and Chow (1994).

Measurements of aerosol composition, size distributions, and aerosol emissions factors have been made in biomass burning plumes either on towers (Susott et al., 1991) or aloft on fixed wing aircraft (e.g., Radke et al., 1991) or on helicopters (e.g., Cofer et al., 1988). As was found for woodstove emissions, the composition of biomass burning emissions is strongly dependent on the stage of combustion (i.e., flaming, smoldering, or mixed), and the type of vegetation (e.g., forest, grassland, scrub). Over 90% of the dry mass in particulate biomass burning emissions is composed of organic carbon (Mazurek et al., 1991). Ratios of organic carbon to elemental carbon are highly variable ranging from 10:1 to 95:1, with the highest ratio found for smoldering conditions and the lowest for flaming conditions. Ambient particle concentrations were about two mg/m^3 during the measurement period. Available measurements suggest that K is by far the most abundant trace element in biomass burning plumes. Although there is considerable inter-sample variation, results from tower samples also suggest that S, Cl,

and K are highest during flaming stages, while Al, Si, Ca, and Fe tend to increase during the smoldering phase (Susott et al., 1991). Emissions factors for total particulate emissions increase by factors of two to four in going from flaming to smoldering stages in the individual fires studied by Susott et al. (1991). These measurements were made when ambient particle concentrations ranged from 15 to 40 mg/m^3.

Particles in biomass burning plumes from a number of different fires were found to have three distinguishable size modes, namely a nucleation mode, an accumulation mode, and a coarse mode (Radke et al., 1991). Based on an average of 81 samples, approximately 70% of the mass was found in particles < 3.5 μm in aerodynamic diameter. The fine particle composition was found to be dominated by tarlike, condensed hydrocarbons and the particles were usually spherical in shape. Additional information for the size distribution of particles produced by vegetation burning was shown in Figure 5-2.

5.2.5   Sea-Salt Production and Other Natural Sources of Aerosol

Although sea-salt aerosol production is confined to salt water bodies, it is included here because many marine aerosols can exert a strong influence on the composition of the ambient aerosol in coastal areas. In some respects, the production of sea-salt aerosols is like that of windblown dust in that both are produced by wind agitation of the surface.   The difference between the two categories arises because sea-salt particles are produced from the bursting of air bubbles rising to the sea surface. Air bubbles are formed by the entrainment of air into the water by breaking waves. The surface energy of a collapsing bubble is converted to kinetic energy in the form of a jet of water which can eject drops above the sea surface. The mean diameter of the jet drops is about 15% of the bubble diameter (Wu, 1979). Bubbles in breaking waves range in size from a few μm to several mm in diameter. Field measurements by Johnson and Cooke (1979) of bubble size spectra show maxima in diameters at around 100 μm, with the bubble size distribution varying as $(d/d_0)^{-5}$ with $d_0 = 100 \ \mu$m.

Since the water jet receives its water from the surface layer, which is enriched in organic compounds, the aerosol drops are composed of this organic material in addition to sea salt (about 3.5% by weight in sea water). Na^+ (30.7%), Cl^- (55.0%), $SO_4^=$ (7.7%), Mg^{2+} (3.6%), Ca^{2+} (1.2%), K^+ (1.1%), HCO_3^- (0.4%), and Br^- (0.2%) are the major ionic species by mass in sea water (Wilson, 1975). The composition of the marine aerosol also reflects the occurrence of

displacement reactions which enrich sea-salt particles in SO_4^- and NO_3^- while depleting them of Cl^- and Br^-. As the drops travel upward above the water surface, they encounter lower relative humidities and lose water until they come into equilibrium with their environment. The resulting marine aerosol size distribution reflects the processes of coagulation, coalescence, and sedimentation.

Seasalt is concentrated in the coarse size mode with a mass median diameter of about 7 μm for samples collected in Florida, the Canary Islands and Barbados (Savoie and Prospero, 1982). The size distribution of sulfate is distinctly bimodal. Sulfate in the coarse mode is derived from sea water but sulfate in the submicron aerosol arises from the oxidation of dimethyl sulfide (CH_3SCH_3) or DMS. DMS is produced during the decomposition of marine micro-organisms. DMS is oxidized to MSA (methane sulfonic acid) a large fraction of which is oxidized to sulfate (e.g., Hertel et al., 1994).

Apart from sea spray, other natural sources of particles include the suspension of organic debris and volcanism. Particles are released from plants in the form of seeds, pollen, spores, leaf waxes and resins, ranging in size from 1 to 250 μm (Warneck, 1988). Fungal spores and animal debris such as insect fragments are also to be found in ambient aerosol samples in this size range. While material from all the foregoing categories may exist as individual particles, bacteria are usually found attached to other dust particles (Warneck, 1988). Smaller bioaerosol particles include viruses, individual bacteria, protozoa, and algae (Matthias-Maser and Jaenicke, 1994). In addition to natural sources, other sources of bioaerosol include industry (e.g., textile mills), agriculture, and municipal waste disposal (Spendlove, 1974).

Trace metals are emitted to the atmosphere from a variety of sources such as sea spray, wind blown dust, volcanoes, wild fires and biotic sources (Nriagu, 1989). Biologically mediated volatilization processes (e.g., biomethylation) are estimated to account for 30-50% of the worldwide total Hg, As, and Se emitted annually, whereas other metals are derived principally from pollens, spores, waxes, plant fragments, fungi, and algae. It is not clear, however, how much of the biomethylated species are remobilized from anthropogenic inputs. Median ratios of the natural contribution to globally averaged total sources for trace metals are estimated to be 0.39 (As), 0.15 (Cd), 0.59 (Cr), 0.44 (Cu), 0.41 (Hg), 0.35 (Ni), 0.04 (Pb), 0.41 (Sb), 0.58 (Se), 0.25 (V), and 0.34 (Zn), suggesting a not insignificant natural source for many trace elements. It

should be noted though that these estimates are based on emissions estimates which have uncertainty ranges of an order of magnitude.

5.3   SOURCES OF SECONDARY PARTICULATE MATTER (SULFUR DIOXIDE, NITROGEN OXIDES, AND ORGANIC CARBON)

Secondary particulate matter is an important contributor to suspended particle mass. Sulfate is formed by the oxidation of SO_2, nitrate by the oxidation of NO_2, and aerosol organic carbon species by the oxidation of a large number of precursors. Thus, the formation rate of a substantial fraction of aerosol mass is given by a complex function of both emission rates of precursor gases and the rates of photochemical processes in the atmosphere. In order to use precursor emissions estimates effectively, however, it is necessary to understand the nature of the processes that cause them to convert to particulate matter. Mechanisms for the oxidation of SO_2 to $SO_4^=$, and NO_2 to NO_3^-, have been discussed in Chapter 3. Both species are oxidized during daytime in the gas phase by hydroxyl (OH) radicals. At night, NO_x is also oxidized to nitric acid by a sequence of reactions initiated by O_3, that include nitrate radicals (NO_3) and dinitrogenpentoxide (N_2O_5). SO_2 is also oxidized by heterogeneous reactions occurring in films of atmospheric particles and in cloud and fog droplets. Data for primary and secondary components of aerosol mass at a number of locations across the United States can be found in Chapter 6.

While the mechanisms and pathways for forming inorganic secondary particulate matter are fairly well known, those for organic secondary aerosol are not well understood. Numerous precursors participate in these conversions, and the rates at which these convert from gas to particles are highly dependent on the concentrations of other pollutants and meteorological conditions. Pandis et al. (1992) identified three mechanisms for secondary organic PM formation: (1) condensation of oxidized end-products of photochemical reactions (e.g., ketones, aldehydes, organic acids, and hydroperoxides); (2) adsorption of organic gases onto existing solid particles (e.g., polycyclic aromatic hydrocarbons); and (3) dissolution of soluble gases which can undergo reactions in particles (e.g., aldehydes). The first and third mechanisms are expected to be of major importance during the summertime when photochemistry is at its peak. The second pathway can be driven by diurnal and seasonal temperature and humidity variations

at any time of the year. Turpin and Huntzicker (1991) and Turpin et al. (1991) provided strong evidence that secondary PM formation occurs during periods of photochemical ozone formation in Los Angeles.

Haagen-Smit (1952) first demonstrated that hydrocarbons irradiated in the presence of NO_x produce light scattering aerosols. Results of later studies summarized by Altshuller and Bufalini (1965) indicated that aerosols are produced by the irradiation of mixtures of NO_x and numerous six-carbon and higher molecular weight acyclic and cyclic olefins and aromatic hydrocarbons. Cyclic olefins were shown to be more effective in aerosol formation than acyclic olefins of similar molecular weight by Stevenson et al. (1965). The possibility that aerosols might be formed from biogenic hydrocarbon emissions was investigated by Went (1960) and Rasmussen and Went (1965). Analyses of the aerosol produced from the photooxidation of α-pinene and NO_x mixtures indicated the presence of pinonic acid and norpinonic acid (Wilson et al., 1972).

Numerous smog chamber studies of the formation of secondary organic aerosol from the photooxidation of terpene precursors have been performed since these earlier studies. A study of the reaction of α-pinene and β-pinene with O_3 by Hatakeyama et al. (1989) obtained aerosol carbon yields (mass of aerosol carbon produced per mass of C reacted), or ACY's, of 18% and 14%, respectively, for HC levels ranging from 10-120 ppb C. In this study, pinonaldehyde, pinenic acid, nor-pinonaldehyde, and nor-pinonic acid accounted for less than 10% of the aerosol yield from the reaction of α-pinene. Hatakeyama et al. (1991) subsequently obtained ACY's of $56 \pm 4\%$ and $79 \pm 8\%$ following the reaction of α-pinene and β-pinene, respectively, for initial HC levels of 820-3170 ppb C and NO_x levels of 210-2550 ppb. Pandis et al. (1991) obtained ACY's ranging from 0.1 to 8% for the oxidation of β-pinene for HC levels ranging from 20-250 ppb C and NO_x levels ranging from 39 to about 700 ppb. Zhang et al. (1992) obtained ACY's ranging from 0 to 5.3% for HC levels ranging from 37-582 ppb C and NO_x levels ranging from 31-380 ppb for the oxidation of α-pinene. Results from the above studies showed that aerosol yields strongly depend on the initial concentration of terpenes and the ratio of hydrocarbons (HC) to NO_x in the reaction chamber. However, Hooker et al. (1985) did not find a significant dependence of aerosol yield on initial HC abundance for HC levels ranging from 3.1-50 ppb C. Their approach differed from that used in all of the above studies because they used ^{14}C-α-pinene. Of the ^{14}C-α-pinene which reacted, 38-68% was found in aerosol

products, 6-20% was found in gas phase products, and 11-29% was lost to the walls of their reaction chamber.

After reaction of the α-pinene with OH radicals or O_3, the radical product will add O_2 to form a peroxy radical. Zhang et al. (1992) proposed that the peroxy radical may react with NO initiating a series of reactions forming pinonaldehyde, which may condense depending on its concentration, or the peroxy radical may react with HO_2 or other free radicals to form aerosol products. The inhibition of the second pathway by the addition of NO was proposed by Zhang et al. (1992) to explain the decrease of aerosol yield with added NO. They also suggested that the dependence of aerosol yield on initial HC concentration arises because the concentration of pinonaldehyde can more easily exceed its saturation value and the rate of formation of aerosol products in the other pathway will also increase.

Pandis et al. (1991) found no aerosol products formed in the photooxidation of isoprene, although they and Zhang et al. (1992) found that the addition of isoprene to reaction mixtures increased the reactivity of the systems studied. Based on their experimental results and the high ratio of terpene to NO_x concentration ratios found in rural and remote areas, Zhang et al. (1992) suggested that the upper limits for aerosol yields they obtained should be used in estimating the aerosol yields from the oxidation of biogenic hydrocarbons.

The aerosol forming potentials of a wide variety of individual anthropogenic and biogenic hydrocarbons were compiled by Pandis et al. (1992) based mainly on estimates made by Grosjean and Seinfeld (1989) and data from Pandis et al. (1991) for β-pinene and Izumi and Fukuyama (1990) for aromatic HC's. The estimates given by Pandis et al. (1992) were converted to aerosol carbon yields below. Examples of compounds with zero ACY's are all C_1-C_7 alkanes, all C_2-C_6 acyclic alkenes, benzene, and aldehydes; examples of compounds with lowest ACY's ($< 2.0\%$) are C_8-C_{10} alkanes, C_6-C_8 cycloalkanes, C_7-C_9 acyclic alkenes, C_5 cyclic alkenes and p-xylene; examples of compounds with intermediate values (2.0%-4.0%) are C_{11}-C_{14} alkanes, C_9-C_{10} cycloalkanes, alkyl benzenes other than p-xylene, C_{10}-C_{13} alkenes and C_6^+ cycloalkenes; and examples of compounds with high values ($>4.0\%$) are C_{15}^+ alkanes, C_{11}^+ cycloalkanes, C_{14}^+ cyclic alkenes and monoterpenes.

Studies of the production of secondary OC in ambient air have focussed on the Los Angeles Basin. Based on aerosol yields shown above, Pandis et al. (1991) suggested that about 1-4 tons day^{-1} of secondary OC in the Los Angeles basin is formed from the oxidation of

monoterpenes which are emitted at the rate of 10-40 tons day[-1]. This estimate may be compared to the secondary OC production rate of 7.5 tons day[-1] estimated to result from the oxidation of anthropogenic hydrocarbons which are emitted at the rate of 1200 tons day[-1] (Grosjean and Seinfeld, 1989). The overall yield of secondary OC from anthropogenic sources in this example is about 0.6%. Pandis et al. (1991) also proposed that most of the secondary OC in highly vegetated urban areas such as Atlanta is produced by the oxidation of monoterpenes.

As part of the Southern California Air Quality Study (SCAQS), Turpin and Huntzicker (1991) measured elemental and organic carbon at Claremont, CA in the summer of 1987 with an in situ carbon analyzer with 2 hour time resolution. During an air pollution episode centered on August 28, 1987, airmass trajectories arriving at Claremont were directed eastward (i.e., inland from the coast), allowing the entrainment of substantial hydrocarbon precursors during transit. Peak OC concentrations (23 μg/m^3) and highest OC to EC ratios (4.6 $\pm$ 0.4) occurred together at Claremont from about 1500 to 1700 PDT. In addition, correlations between EC and OC were low throughout the day (R^2 =0.38). Turpin and Huntzicker (1991) also measured OC and EC concentrations at Long Beach in November of 1987 with the same instrumentation. On the basis of these data, they suggested that OC to EC ratios of 2.2 $\pm$ 0.7 are characteristic of primary OC in the Los Angeles area.

Pandis et al. (1992) constructed a Lagrangian trajectory model to simulate the chemical formation, transport and deposition of secondary OC during the August episode. They used estimates of aerosol yields from HC oxidation compiled by Grosjean and Seinfeld (1989), updated as necessary (e.g., Pandis et al., 1991) along with estimates of daily emissions, to predict that 28% of the peak secondary OC on Aug. 28 at Claremont resulted from the oxidation of toluene, 38% from other aromatic HC's, 9% from biogenic HCs, 21% from alkanes and cycloalkanes, and the remaining 4% from other species. Values were somewhat different on a daily average basis (19% from toluene, 46% from other aromatic HC's, 16% from biogenic HC's, 15% from alkanes, and 4% from alkenes). There was reasonable agreement with the data of Turpin and Huntzicker (1991) throughout most of the day, but calculated peak secondary OC levels (~5 μg/m^3) were about half those inferred by Turpin and Huntzicker (1991). A combination of factors could have contributed to this underprediction including errors in emissions, deposition rates, chemical reaction rate data and aerosol yields. In general, the calculated secondary OC represented 15-27% of the daily average total OC at inland locations

(Burbank, Claremont, Azusa, and Rubidoux) on August 28, 1987 and 5-19% of the average total OC at coastal sites.

Attempts were made during SCAQS to determine the composition of the organic carbon fraction of the ambient aerosol. Organic nitrates were measured on size segregated samples collected on zinc selenide disks which were later analyzed by transmission FTIR by Mylonas et al. (1991). Concentrations of organic nitrates in the particle phase ranged from 0.8 to 4.0 $\mu g/m^3$, with maximum mass loadings in the 0.05 to 0.075 μm and 0.12 to 0.26 μm size ranges. Concurrently, Pickle et al. (1990) used infrared spectroscopy to measure the total abundance of compounds containing carbonyl groups and aliphatic compounds. Maximum absorption at wavelengths characteristic of carbonyl groups was observed for particles in the 0.12 to 0.26 μm and 0.5 to 1.0 μm size ranges. These results suggest that carbonyl compounds are largely of secondary origin and that IR absorption by aliphatic compounds in particles smaller than 0.12 μm was correlated directly with automotive emissions.

Kao and Friedlander (1995) examined the statistical properties of a number of PM components in the South Coast Air Basin. They found that the concentrations of non-reactive, primary components of PM_{10} have approximately log normal frequency distributions and constant values of geometric standard deviations (GSDs) regardless of source type and location within their study area. However, aerosol constituents of secondary origin (e.g., $SO_4^=$, NH_4^+, and NO_3^-) were found to have much higher GSD's. Surprisingly, the GSD's of organic (1.87) and elemental (1.74) carbon were both found to be within 1σ (0.14) of the mean GSD (1.85) for non-reactive primary species, compared to GSD's of 2.1 for sulfate, 3.5 for nitrate, and 2.6 for ammonium. These results suggest that most of the OC seen in ambient samples is of primary origin. Pinto et al. (1995) found similar results for data obtained during the summer of 1994. Further studies are needed to determine if these relations are valid at other locations and to determine to what extent the results might be influenced by the evaporation of volatile constituents after sampling.

It must be emphasized that the inferences drawn from field studies in the Los Angeles Basin are unique to that area and cannot be extrapolated to other areas of the country. In addition, there is a high degree of uncertainty associated with all aspects of the calculation of secondary OC concentrations which is compounded by the volatilization of OC during and after sampling. Grosjean and Seinfeld (1989) derived a factor of five range in estimates of production

rates of secondary OC in the Los Angeles area by comparison of results obtained from four different methods. Aerosol yields from the oxidation of individual hydrocarbons reported by different investigators vary by an order of magnitude (Grosjean and Seinfeld, 1989). Significant uncertainties always arise in the interpretation of smog chamber data because of wall reactions. Limitations also exist in extrapolating the results of smog chamber studies to ambient conditions found in urban airsheds and forest canopies. Concentrations of terpenes and NO_x are much lower in forest canopies (Altshuller, 1983) than are commonly used in smog chamber studies. The identification of aerosol products of terpene oxidation has not been a specific aim of field studies, making it difficult to judge the results of model calculations of secondary OC formation. Uncertainties may also arise because of the methods used to measure biogenic hydrocarbon emissions. Khalil and Rasmussen (1992) found much lower ratios of terpenes to other hydrocarbons (e.g., isoprene) in forest air than were expected, based on their relative emissions strengths and rate coefficients for reaction with OH radicals and O_3. They offered two explanations, either the terpenes were being rapidly removed by some heterogeneous process or emissions were artificially enhanced by feedbacks caused by the bag enclosures they used. If the former consideration is correct, then the production of aerosol carbon from terpene emissions could be substantial; if the latter is correct, then terpene emissions could have been overestimated by the techniques used.

5.4 EMISSIONS ESTIMATES FOR PRIMARY PARTICULATE MATTER AND SO_2, NO_x, AND VOCs IN THE UNITED STATES

The emissions of a pollutant can be expressed by the following equation:

$$E = \sum_i A_i.F_i.(1-C_{eff,i}) \tag{5-1}$$

where E is the total emissions rate from all sources; A_i is the activity rate for source i; F_i is the emissions factor for the production of the pollutant by source i; and $C_{eff,i}$ is the fractional efficiency of control devices used by source i. Activity rates relevant to the entries shown in Tables 5-6 to 5-10 might refer to the electricity generated by power plants, the amount of coke produced by a coke oven, the distance travelled by motor vehicles, the amount of biomass

consumed by forest fires per year, etc. The mass of pollutant emitted per unit activity of a source is then expressed in terms of an emissions factor (e.g., amount of NO_x emitted per kw-hour of energy generated or per vehicle mile travelled). Emissions factors are given in compilations (e.g., AP-42 [U.S. Environmental Protection Agency, 1995a]) or are calculated by emissions models, which include a number of variables which can affect emissions. Examples include the U.S. Environmental Protection Agency's PART5 model for estimating particulate motor vehicle emissions, and BEIS which is used to calculate emissions of hydrocarbons from vegetation (Geron et al., 1994). The product of $A_i \times F_i$ yields an estimate of the uncontrolled emissions from a particular source i. These are then multiplied by a factor incorporating the effects of any control devices that might be used. It is acknowledged that control equipment breaks down, and its efficiency might not be maintained over its lifetime of operation. Therefore, the optimum efficiencies of control devices are multiplied by a rule effectiveness factor. The default value for the rule effectiveness factor is taken to be 0.8 in the inventory calculations, unless a better factor can be justified (U.S. Environmental Protection Agency, 1989). Equation 5-1 was used in the preparation of the emissions inventories shown in Tables 5-6 through 5-10. Further details about collection and reporting methods may be found in the National Emissions Inventory Trends data base (U.S. Environmental Protection Agency, 1994).

Table 5-6 shows the primary PM_{10} emissions estimated for the period of 1985 through 1993 using the National Emissions Inventory Trends data base (U.S. Environmental Protection Agency, 1994). Emissions are shown in the original units used in their calculation. A short ton is equal to 2,000 pounds or 9.08×10^5 gm. Between 1985 and 1993, PM_{10} emissions from stationary and mobile sources decreased almost 10 percent. During this period, contributions from highway vehicles decreased by 27 percent, reflecting emissions controls on diesel vehicles. Contributions from industrial fuel production

**TABLE 5-6. NATIONWIDE PRIMARY PM$_{10}$ EMISSION ESTIMATES FROM
MOBILE AND STATIONARY SOURCES, 1985 TO 1993**

Source Category				(Thousands short tons/year)				
	1985	1986	1987	1988	1989	1990	1991	1992	1993
Fuel Combustion - Electric Utilities	284	289	282	278	278	291	253	255	270
Fuel Combustion - Industrial	234	231	226	230	229	228	229	223	219
Fuel Combustion - Other	896	902	910	918	922	930	942	819	723
Chemical and Allied Product Manufacturing	67	68	68	73	74	74	72	75	75
Metals Processing	147	137	131	141	142	140	136	137	141
Petroleum and Related Industries	32	31	30	29	28	28	28	27	26
Other Industrial Processes	317	321	314	314	308	306	300	303	311
Solvent Utilization	2	2	2	2	2	2	2	2	2
Storage and Transport	57	56	54	54	54	54	53	53	55
Waste Disposal and Recycling	279	275	265	259	251	242	245	246	248
Highway Vehicles	271	265	261	256	253	239	223	210	197
Off-Highway	368	372	350	387	372	372	367	379	395
Total	2,953	2,949	2,893	2,942	2,909	2,907	2,849	2,729	2,661

Note: The sums of sub-categories may not equal total due to rounding (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1994).

TABLE 5-7. MISCELLANEOUS AND NATURAL SOURCE PRIMARY PM$_{10}$ EMISSION ESTIMATES, 1985 TO 1993

Source Category	(Thousands short tons/year)								
	1985	1986	1987	1988	1989	1990	1991	1992	1993
Fugitive Dust									
Unpaved roads	14,719	14,672	13,960	15,626	15,346	15,661	14,267	14,540	14,404
Paved roads	6,299	6,555	6,877	7,365	7,155	7,299	7,437	7,621	8,164
Construction/mining and quarrying	13,009	12,139	12,499	12,008	11,662	10,396	10,042	10,899	11,368
Agriculture and Forestry									
Agricultural crops	6,833	6,899	7,008	6,090	6,937	6,999	6,965	6,852	6,842
Agricultural livestock	275	285	330	376	397	381	363	386	394
Other Combustion									
Wildfires	142	142	142	142	142	717	457	341	418
Managed burning	523	530	536	555	549	546	537	547	549
Other	59	59	59	59	59	59	59	59	59
Natural Sources wind erosion	3,565	9,390	1,457	17,509	11,862	4,192	10,054	4,655	628
Total	45,424	50,671	42,868	60,730	54,073	46,250	50,181	45,900	42,826

Note: The sums of sub-categories may not equal total due to rounding (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1994).

TABLE 5-8. NATIONWIDE SULFUR OXIDES EMISSION ESTIMATES, 1984 TO 1993

Source Category	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
					(Thousands short tons/year)					
Fuel Combustion - Electric Utilities	16,023	16,273	15,701	15,715	15,990	16,218	15,898	15,784	15,417	15,836
Fuel Combustion - Industrial	2,723	3,169	3,116	3,068	3,111	3,086	3,106	3,139	2,947	2,830
Fuel Combustion - Other	728	578	611	663	660	623	597	608	600	600
Chemical and Allied Product Manufacturing	229	456	432	425	449	440	440	442	447	460
Metals Processing	1,387	1,042	888	616	702	657	578	544	557	580
Petroleum and Related Industries	707	505	469	445	443	429	440	444	417	409
Other Industrial Processes	923	425	427	418	411	405	401	391	401	413
Solvent Utilization	0	1	1	1	1	1	1	1	1	1
Storage and Transport	0	4	4	4	5	5	5	5	5	5
Waste Disposal and Recycling	25	34	35	35	36	36	36	36	37	37
Highway Vehicles	445	446	449	457	468	480	480	478	483	438
Off-Highway	198	208	221	233	253	267	265	266	273	278
Miscellaneous	9	7	7	7	7	7	14	11	10	11
Total	23,396	23,148	22,361	22,085	22,535	22,653	22,261	22,149	21,592	21,888

Note: The sums of sub-categories may not equal the totals, due to rounding (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1994).

TABLE 5-9. NATIONWIDE NO$_x$[a] EMISSION ESTIMATES, 1984 TO 1993

					(Thousands short tons/year)					
Source Category	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
Fuel Combustion - Electric Utilities	7,268	6,916	9,909	7,128	7,530	7,607	7,516	7,482	7,473	7,782
Fuel Combustion - Industrial	3,415	3,209	3,065	3,063	3,187	3,209	3,256	3,309	3,206	3,176
Fuel Combustion - Other	670	701	694	710	737	730	732	745	735	732
Chemical and Allied Product Manufacturing	161	374	381	371	398	395	399	401	411	414
Metals Processing	54	87	80	76	82	83	81	79	80	82
Petroleum and Related Industries	70	124	109	101	100	97	100	103	96	95
Other Industrial Processes	203	327	328	320	315	311	306	298	305	314
Solvent Utilization	0	2	3	3	3	3	2	2	3	3
Storage and Transport	0	2	2	2	2	2	2	2	3	3
Waste Disposal and Recycling	90	87	87	85	85	84	82	81	83	84
Highway Vehicles	8,387	8,089	7,773	7,662	7,661	7,662	7,488	7,373	7,440	7,437
Off-Highway	2,644	2,734	2,777	2,664	2,914	2,844	2,843	2,796	2,885	2,966
Miscellaneous	210	201	202	203	206	205	384	305	272	296
Total	23,172	22,853	22,409	22,386	23,221	23,250	23,192	22,977	22,991	23,402

[a]Emissions calculated as NO_2.

Note: The sums of sub-categories may not equal total due to rounding (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1994).

TABLE 5-10. NATIONWIDE VOLATILE ORGANIC COMPOUND EMISSION ESTIMATES, 1984 TO 1993

					(Thousands short tons/year)					
Source Category	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
Fuel Combustion - Electric Utilities	45	32	34	34	37	37	36	36	35	36
Fuel Combustion - Industrial	156	248	254	249	271	266	266	270	271	271
Fuel Combustion - Other	917	508	499	482	470	452	437	426	385	341
Chemical and Allied Product Manufacturing	1,620	1,579	1,640	1,633	1,752	1,748	1,771	1,778	1,799	1,811
Metals Processing	182	76	73	70	74	74	72	69	72	74
Petroleum and Related Industries	1,253	797	764	752	733	731	737	745	729	720
Other Industrial Processes	227	439	445	460	479	476	478	475	482	486
Solvent Utilization	6,309	5,779	5,710	5,828	6,034	6,053	6,063	6,064	6,121	6,249
Storage and Transport	1,810	1,836	1,767	1,893	1,948	1,856	1,861	1,868	1,848	1,861
Waste Disposal and Recycling	687	2,310	2,293	2,256	2,310	2,290	2,262	2,217	2,266	2,271
Highway Vehicles	9,441	9,376	8,874	8,201	8,290	7,192	6,854	6,499	6,072	6,094
Off-Highway	1,973	2,008	2,039	2,038	2,106	2,103	2,120	2,123	2,160	2,207
Miscellaneous	951	428	435	440	458	453	1,320	937	780	893
Total	25,572	25,417	24,826	24,338	24,961	23,731	24,276	23,508	23,020	23,312

Note: The sums of sub-categories may not equal total due to rounding (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1994).

decreased by 6 percent, leading to an overall decrease of about 10% in emissions from all of these categories from 1985 to 1993.

Table 5-7 shows PM_{10} emissions from natural and miscellaneous sources for 1985 to 1994. Fugitive dust is the largest source in the miscellaneous category. No clear trend is evident in overall fugitive dust emissions, because increases in paved road dust are offset by decreases in the mining and quarrying and construction categories. The large year-to-year variability in wind erosion reflects changes in precipitation and regional soil conditions. For instance, the values for 1993 reflect the flooding and extremely wet conditions that occurred in the midwestern United States.

Tables 5-8 through 5-10 show nationwide emissions for sulfur dioxide, oxides of nitrogen, and VOC's, which are all precursors for secondary aerosol formation, for the period from 1984 through 1993. Electric utilities account for the largest fraction of sulfur dioxide, nearly 70% of total emissions in 1993 (Table 5-8). Estimates of sulfur dioxide emissions from industrial fuel combustion increased by approximately 16% from 1984 to 1985, and decreased by 11% between 1985 and 1993. Sulfur dioxide emissions from chemical manufacturing doubled between 1984 and 1985, with emissions leveling off between 0.42 and 0.46 million short tons/year after 1985. Sulfur dioxide emissions from highway vehicles were estimated to have increased by 8% from 1984 to 1989, then levelling off and then decreasing by about 10% from 1992 to 1993, reflecting the introduction of regulations for the desulfurization of diesel fuel. Off-highway vehicle emissions increased from 0.20 million short tons per year in 1984 to 0.28 million short tons per year in 1993. Major sulfur dioxide emissions reductions were observed for petroleum processing and other industrial processes, with decreases of 40% to 50% over the ten-year period. In total, however, sulfur dioxide emissions estimates in 1993 decreased by 6% from those given for 1984.

Table 5-9 shows no significant variations in total nitrogen oxides emissions over the 10-year period. Electric utility and motor vehicle emissions each account for about one-third of total emissions. Emissions from (a) industrial and other fuel combustion and (b) from off-highway vehicles each account for about one-sixth of total emissions. There is little change in total emissions from 1984 to 1993. Moderate increases are seen in the electric utility, industrial and other fuel combustion, and off-highway vehicles categories with much larger

relative increases for chemical manufacturing and metals processing. These increases are offset by decreases in fuel combustion by industry and on-highway vehicles.

Volatile organic compound (VOC) emissions in Table 5-10 are dominated by highway vehicles and solvent use. These two sources together account for 50 to 60% of total emissions. Off-highway vehicles, petroleum-related industries, chemical manufacturing, and petroleum storage and transport account for most of the remaining amounts. VOC emissions from highway vehicles were reduced between 1984 and 1993 by 35%, in spite of increased vehicle mileage. Most of this decrease is due to the presumed effectiveness of emissions controls on newer vehicles. VOC emissions from petroleum industries also were reduced by 43% between 1984 and 1993. Total VOC emissions decreased by 9% between 1984 and 1993. It should be noted that emissions from natural sources are not reflected in the above discussion.

Although total emissions of gaseous precursors (SO_2, NO_x, and VOC's) are shown in Tables 5-8, 5-9, and 5-10, it should be remembered that these values cannot be directly translated into production rates of particulate matter. Dry deposition and precipitation scavenging of some of these gases can occur before they are oxidized to aerosols in the atmosphere. In addition, some fraction of these gases are transported outside of the domain of the continental United States before being oxidized. Likewise, emissions of these gases from areas outside the United States can result in the transport of their oxidation products into the United States. While the chemical oxidation of SO_2 will lead quantitatively to the formation of $SO_4^=$, the formation of aerosol from the oxidation of VOC's will be much less because only a small fraction of VOC's react to form particles, and those that do have efficiencies less than 10% (c.f. Section 5.3). The oxidation of NO_2 will yield HNO_3, some of which may dry deposit or be scavenged by precipitation, and the remainder will form particulate nitrate.

Projections of future emissions of primary PM_{10}, SO_2, and NO_x are shown in Table 5-11. Controls mandated by the Clean Air Act Amendments of 1990 are expected to reduce PM_{10} emissions in nonattainment areas. However, because emissions in nonattainment areas constitute a small subset of total emissions, overall emissions are projected as still likely to increase. Fugitive dust sources contribute the major share of the increase. Changes in emissions after 1996 solely reflect activity level changes with the

TABLE 5-11. PROJECTED TRENDS IN PARTICULATE MATTER (PM$_{10}$), SULFUR DIOXIDE (SO$_2$), AND OXIDES OF NITROGEN (NO$_x$) EMISSIONS (10^6 short tons yr^{-1})

| | | | PM$_{10}$ Source Categories | | | | | | | | |
| | | | Fuel Combustion[a] | | | | Mobile[a] | | | | |
	Natural[a]	Misc.[a,b]	Electric Utilities	Industrial	Other	OS	On-Road	Nonroad	Total	SO$_2$[d]	NO$_x$[d]
1990	4.36	36.3	0.28	0.24	0.55	0.90	0.36	0.37	43.3	22.4	23.0
1993	1.98	37.9	0.26	0.23	0.54	0.91	0.32	0.40	42.5	21.5	23.3
1996	4.36	43.6	0.31	0.21	0.66	0.89	0.15	0.44	50.6	18.1	21.9
1999	4.36	48.5	0.33	0.20	0.59	0.93	0.13	0.47	55.9	17.6	21.8
2000	4.36	49.8	0.34	0.20	0.66	0.94	0.12	0.48	56.9	17.4	20.5
2002	4.36	51.8	0.35	0.19	0.59	0.97	0.13	0.50	59.0	17.1	20.5
2005	4.36	54.9	0.37	0.19	0.64	1.01	0.13	0.53	62.2	16.7	20.8
2008	4.36	57.4	0.40	0.18	0.69	1.04	0.13	0.55	64.7	16.1	21.3
2010	4.36	59.0	0.42	0.18	0.73	1.06	0.12	0.56	66.4	15.7	21.6

[a]Same categories as used in Tables 5-6 and 5-7.
[b]The miscellaneous category includes fugitive dust from unpaved and paved roads, and other sources; wildfires and managed burning; and agricultural and forestry related emissions.
[c]OS refers to other stationary sources such as chemical manufacturing, metal processing, petroleum refining, other industrial processes, solvent utilization, storage and transport, waste disposal and recycling.
[d]Only total emissions are shown.

Source: U.S. Environmental Protection Agency (1995b).

exception of on-road vehicles. Emission factors for on-road vehicles are expected to decrease

mainly because of stringent standards for diesel emissions. Diesel vehicle emissions are

expected to decrease nationwide by about 70% from 1990 to 2010 (U.S. Environmental

Protection Agency, 1993). This decrease results mainly from a roughly 90% decrease in

emissions factors which are partially offset by an increase in total diesel vehicle miles travelled.

As can be seen from Table 5-11, emissions from non-road sources (e.g., marine vessels,

railroads, aircraft, vehicles used in construction, industry, agriculture, airport services, and

landscaping) are projected to exceed those from on-road vehicles from 1990 to 2010.

Emissions of SO_2 from fossil fuel combustion by electric utilities show an expected

continued decline through 2010. Emissions from all other categories in Table 5-7 show a slight

increase from 1993 to 2002 and then level off to the year 2010. Total NO_x emissions show a

decrease of over 10% from 1993 to 2002, then increase by about 5% by the year 2010. This

pattern reflects projected emissions for the major categories of fuel combustion by electric

utilities and on-road vehicles.

Emissions of ammonia and ammonium are not included in the U.S. Environmental

Protection Agency inventories for criteria pollutants. Dentener and Crutzen (1994) have

constructed a global inventory of NH_3 emissions. Anthropogenic sources (animals kept for

human use, fertilizer applications, and biomass burning) and natural sources (wild animals,

vegetation, and the oceans) were included. Emissions from sewage were not included, though.

Vegetation was found to be either a source or a sink for NH_3 depending on ambient

concentrations and vegetation type. Animals kept for human use represent the largest single

source category. Highest emission rates in North America were found in the central United

States. Matthews (1994) found that about 75% of U.S. NH_3 emissions from the application of

nitrogenous fertilizers occur in the central United States, with the remainder about evenly

divided between the eastern and western United States. Emissions of approximately 0.51 Tg

NH_3-N yr^{-1} were calculated for the United States. The Dentener and Crutzen (1994) estimate of

NH_3 emissions for North America of 5.2 Tg N yr^{-1} may be compared to a wet deposition rate of

NH_4^+ in the United States of 3 -4.5 Tg N yr^{-1}, and three separate emission inventories yielding

values of 1.2, 8.8, and 2.8 Tg N yr^{-1} for the U.S. (Placet et al., 1991).

While emissions of organic carbon (OC) and elemental carbon (EC) are included implicitly

in the emissions inventories for PM_{10}, it is still useful to consider independent estimates. Zhang

et al. (1992) estimated the total production of secondary organic aerosol to be about 1.2 Tg yr^{-1} in the United States. Liousse et al. (1996) have constructed OC and EC emissions inventories for use in a global scale chemical tracer model. They estimate OC emissions of 0.80 Tg OC yr^{-1} from live biomass combustion, 1.4 Tg OC yr^{-1} from fossil fuel combustion, and 0.59 Tg OC yr^{-1} from the oxidation of naturally emitted terpenes assuming a fractional aerosol yield of 5%. Carbon values for OC sources have been multiplied by a factor of 1.2 to account for the presence of oxidized species. EC emissions from the combustion of live biomass and fossil fuels are estimated to be 0.11 Tg EC yr^{-1} and 0.30 Tg C yr^{-1}, respectively. These estimates are roughly 8% of total particulate emissions shown in Tables 5-6 and 5-7. Comparisons of model results with observations from the IMPROVE/NESCAUM network by Liousse et al. (1996) suggest that both the OC and EC emissions derived for their model may be systematically underestimated by at least a factor of two.

The regional nature of total primary particulate matter emissions is illustrated in Figure 5-5. At least 80% of the emissions in any single region arises from fugitive dust sources and wind erosion. SO$_2$ regional emissions are shown in Figure 5-6 as a reminder that they are highest in the eastern United States and that the oxidation of SO$_2$ to SO$_4^=$ can constitute a substantial fraction of the aerosol mass in the eastern United States. It can also be seen that the ratio of SO$_2$ to primary PM$_{10}$ emissions tends to be much higher in the eastern than in the western United States.

Annual averages do not reflect the seasonality of certain emissions. Residential wood burning in fireplaces and stoves, for example, is a seasonal practice which reaches its peak during cold weather. Cold weather also affects motor vehicle exhaust particulate emissions, both in terms of chemical composition and emission rates (e.g., Watson et al., 1990b; Huang et al., 1994). Planting, fertilizing, and harvesting are also seasonal activities. Forest fires occur mainly during the local dry season and during periods of drought.

Several of the sources in Tables 5-6 through 5-10 are episodic rather than continuous in nature. This is especially true of prescribed and structural fires and fugitive dust emissions. Although windblown dust emissions are low on an annual average, they are likely to be quite
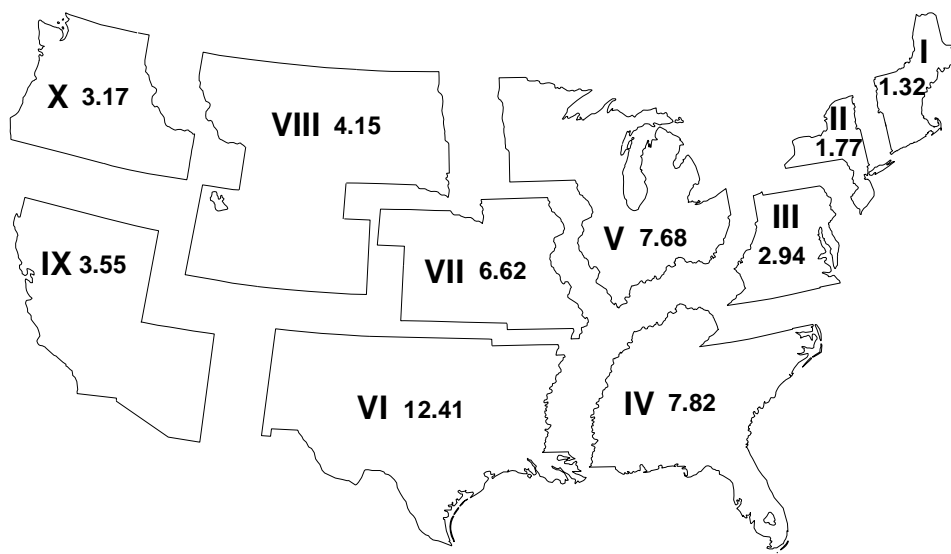
Figure 5-5. **Estimates of primary PM$_{10}$ emissions by U.S. Environmental Protection Agency region for 1992.**

Units = 10^6 short tons/yr (1 short ton = 9.08×10^5 gms).

Source: U.S. Environmental Protection Agency (1993).
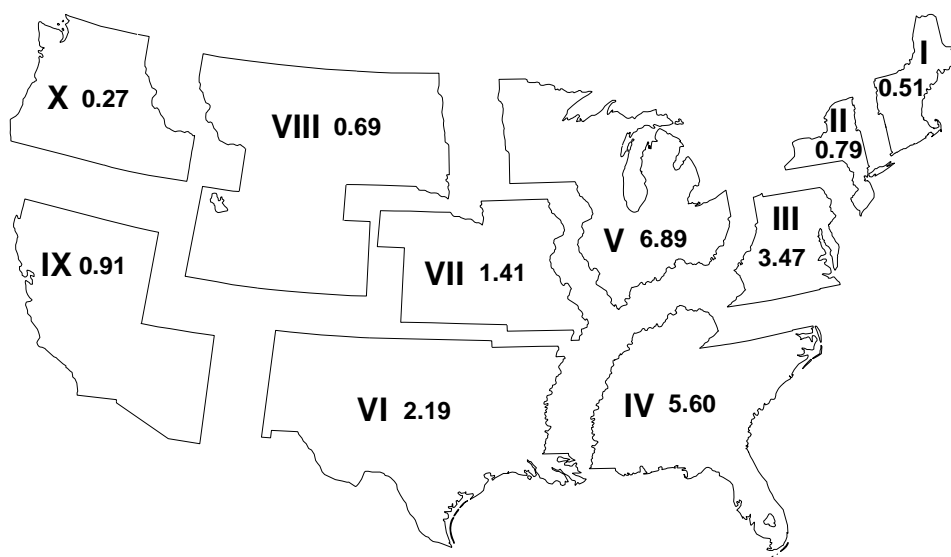
Figure 5-6. **Estimates of sulfur dioxide emissions by U.S. Environmental Protection Agency region for 1992.**

Units = 10^6 short tons/yr (1 short ton = 9.08×10^5 gms).
Source: U.S. Environmental Protection Agency (1993).

large during those few episodes when wind speeds are high. The transport of Saharan dust to the continental United States is also highly episodic.

5.5   APPLICATIONS AND LIMITATIONS OF EMISSIONS INVENTORIES AND RECEPTOR MODELS

This section examines requirements for the design and construction of emissions inventories and potential areas of uncertainty and limitations in their use. Receptor modeling methods to apportion sources to mass components in ambient aerosol measurements, and results for a number of aerosol monitoring studies, will then be presented. Some general considerations of the relative strengths and weaknesses of using emissions inventories and receptor models to assign sources to particulate matter components in ambient samples will then be discussed. Finally, results from specific receptor modeling studies in the eastern and western United States will be discussed.

5.5.1   Uncertainties in Emissions Estimates

It is difficult to assign uncertainties quantitatively to entries in emissions inventories. Methods that can be used to verify or place constraints on emissions inventories are sparse. In general, the overall uncertainty in the emissions of a given pollutant includes contributions from all of the terms on the right hand side of Eq. 5-1 (activity rates, emissions factors, and control device efficiencies). Additional uncertainties can arise during the compilation of an emissions inventory because of missing sources and arithmetical errors. The variability of emissions can cause errors when annual average emissions are applied to applications involving shorter time scales.

Activity rates for well-defined point sources (e.g., power plants) should have the smallest uncertainty associated with their use, since accurate production records need to be kept. On the other hand, activity rates for a number of areally dispersed fugitive sources are extremely difficult to quantify. Emissions factors for easily measured fuel components which are quantitatively released during combustion (e.g., CO_2 and SO_2) should be the most reliable. Emissions of components formed during combustion are more difficult to characterize as the

emissions rates are dependent on factors specific to individual combustion units and on combustion stage (i.e., smoldering or active). Although the AP-42 emissions factors (U.S. Environmental Protection Agency, 1995a) contain extensive information for a large number of source types, these data are very limited in the number of sources sampled. The efficiency of control devices is determined by their age, their maintenance history, and operating conditions. It is virtually impossible to assign uncertainties in control device performance due to these factors. It should be noted that the largest uncertainties occur for those devices which have the highest efficiencies (>90%). This occurs because the efficiencies are subtracted from one and small errors in assigning efficiencies can lead to large errors in emissions.

Ideally an emissions inventory should include all major sources of a given pollutant. This may be an easy task for major point sources, but becomes problematic for poorly characterized area sources. As an example, it was recently realized that meat cooking could be a significant source of organic carbon (Hildemann et al., 1991). Further research is needed to better characterize the sources of pollutants in order to reduce this source of uncertainty. Errors can arise from the misreporting of data, and arithmetic errors can occur in the course of compiling entries from thousands of individual sources. A quality assurance program is required to check for outliers and arithmetic errors.

Because of the variability in emissions rates, there can be errors in the application of inventories developed on an annually averaged basis (as are the inventories shown in Tables 5-6 to 5-10) to episodes occurring on much shorter time scales. As an example, most modeling studies of air pollution episodes are carried out for periods of a few days.

Uncertainties in annual emissions were estimated to range from 4 to 9% for SO_2 and from 6 to 11% for NO_x in the 1985 NAPAP inventories for the United States (Placet et al., 1991). Uncertainties in these estimates increase as the emissions are disaggregated both spatially and temporally. The uncertainties quoted above are conservative estimates and refer only to random variability about the mean, assuming that the variability in emissions factors was adequately characterized and that extrapolation of emissions factors to sources other than those for which they were measured is valid. The estimates do not consider the effects of weather or variations in operating and maintenance procedures. Fugitive dust sources, as mentioned above, are extremely difficult to quantify, and stated emission rates may only represent order-of-magnitude estimates. As rough estimates, uncertainties in emissions

estimates could be as low as 10% for the best characterized source categories, while emissions figures for windblown dust should be regarded as order-of-magnitude estimates. Given (a) uncertainties in the deposition of SO_2 and its oxidation rate, (b) the variability seen in OC and EC emissions from motor vehicles along with the findings from past verification studies for NMHC and CO to NO_x ratios, (c) ranges of values found among independent estimates for emissions of individual species (NH_3, OC), and (d) the predominance of fugitive emissions, PM emissions rates should be regarded as order-of-magnitude estimates.

There have been few field studies designed to test emissions inventories observationally. The most direct approach would be to obtain cross-sections of pollutants upwind and downwind of major urban areas from aircraft. The computed mass flux through a cross section of the urban plume can then be equated to emissions from the city chosen. This approach has been attempted on a few occasions. Results have been ambiguous because of contributions from fugitive sources, non-steady wind flows, and general logistic difficulties.

Greater success, albeit on a smaller scale, has been achieved in studies that tested predictions of the State of California EMFAC emissions model. An ambient-air study in the Los Angeles basin (Fujita et al., 1992) showed that motor vehicle emissions of CO and nonmethane hydrocarbons (NMHC) were being systematically underpredicted in the emissions model by a factor of about 2.5, assuming that NO_x emissions were much better known; i.e., the CO to NO_x and NMHC to NO_x ratios were underpredicted by the model. A study performed in a tunnel in the Los Angeles basin (Ingalls, 1989; Pierson et al., 1990) showed that motor vehicle NO_x emission rates (g/mi) were predicted approximately correctly but that the CO and NMHC emission rates were systematically underpredicted in the emissions model by factors of two to three. Similar tests need to be performed for particulate matter emissions from motor vehicles.

A completely different approach to obtaining area-wide emissions of pollutants relies on the construction of inversion algorithms applied in the context of atmospheric transport models (Brown, 1993). Emissions of a pollutant that are required to produce a specified distribution of surface concentrations are solved for by using model-derived transport and chemical loss terms. Uncertainties in the emissions fields are then generated in terms of specified uncertainties in the observed data and in the model transport and chemistry fields.

A number of factors limit the ability of an emissions inventory driven, chemical tracer model to determine the effects of various sources on particle samples obtained at a particular location apart from uncertainties in the inventories given above. Air pollution model predictions represent averages over the area of a grid cell, which in the case of the Urban Airshed Model typically has been 25 km^2 (5 km × 5 km). The contributions of sources to pollutant concentrations at a monitoring site are strongly controlled by local conditions which cannot be resolved by an Eulerian grid-cell model. Examples would be the downward mixing of tall stack emissions and deviations from the mean flow caused by buildings. The impact of local sources may not be accurately predicted, because their emissions would be smeared over the area of a grid cell or if the local wind flow were in the wrong direction during sampling.

For these reasons, receptor models have been used to determine source contributions to particulate matter at individual monitoring sites. Receptor models are strictly diagnostic in their application and do not have the prognostic, or predictive, capability of chemical transport models. In addition, receptor models have been developed for apportioning sources of primary particulate matter and are not formulated to include the processes of secondary particulate matter formation which are explicitly included in the chemical transport models.

5.5.2   Receptor Modeling Methods

Receptor models relate source contributions to ambient concentrations based on composition analysis of ambient particulate samples. They depend on the assumption of mass conservation and the use of a mass balance. As an example, assume that the total concentration of particulate lead measured at a site can be considered to be the sum of contributions from a number of independent sources,

$$Pb_{total} = Pb_{motor\ vehicles} + Pb_{soil} + Pb_{smelter} + \ . \ . \ . \tag{5-2}$$

Since most sources emit particles that contain a number of chemical elements or compounds, the atmospheric concentration of an element can be considered to be the product of the abundance of the element of interest (ng/mg) in the effluent and the mass concentration of particles from that source in the atmosphere (mg/m^3). For lead from motor vehicles, for example,

$$Pb_{motor\ vehicles} = a_{Pb,\ mv}\ f_{mv} \qquad (5\text{-}3)$$

where $a_{Pb,mv}$ is the abundance of lead in motor vehicle emissions, and f_{mv} is the mass concentration of motor vehicle emitted particles in the atmosphere. Extending this idea to m chemical elements, n samples, and p independent sources,

$$x_{ij} = \sum_{k=1}^{p} a_{ik}\ f_{kj} \qquad (5\text{-}4)$$

where x_{ij} is the ith elemental concentration measured in the jth sample (ng m^{-3}), a_{ik} is the gravimetric abundance of the ith element in material from the kth source (ng mg^{-1}), and f_{kj} is the airborne mass concentration of material from the kth source contributing to the jth sample (mg m^{-3}). The f_{kj} are the quantities to be determined from Equation 5-4. To distinguish the contributions of one source type from another using receptor models, the chemical and physical characteristics must be such that (1) they are present in different proportions in different source emissions, (2) these proportions remain relatively constant for each source type, and (3) changes in these proportions between source and receptor are negligible or can be empirically represented.

A number of specialty conference proceedings, review articles, and books have been published to provide greater detail about source apportionment receptor models (Cooper and Watson, 1980; Watson et al., 1981; Macias and Hopke, 1981; Dattner and Hopke, 1982; Pace, 1986; Watson et al., 1989; Gordon, 1980, 1988; Stevens and Pace, 1984; Hopke, 1985, 1991; Javitz et al., 1988). Watson et al. (1994b) present data analysis plans which include receptor models as an integral part of visibility and PM$_{10}$ source apportionment and control strategy development.

The first step in attempting to relate ambient particulate matter measured at a particular location to source contributions is typically data evaluation. The objectives for data evaluation are: (1) to summarize the accuracy and precision of measurements; (2) to identify and investigate extreme and inconsistent values; (3) to perform data comparisons and investigate discrepancies; and (4) to estimate the equivalence of measurements of the same variable by different methods. Even with the most stringent quality assurance, it is prudent to perform several straightforward analyses to identify the presence of any discrepancies in atmospheric

particulate data and to correct, flag, or eliminate them. Investigating the equivalence of different measurement methods for the same variable is especially important for particulate chemical measurements, which may show substantial differences in concentration depending upon how they were made. Data evaluation activities include: (1) plotting and examining pollutant time series data to identify spikes and outliers for investigation; (2) comparing the sum of chemical species with PM_{10} mass measurements; and (3) comparing measurements of the same variables at the same or nearby sites using different measurement devices and procedures.

After data evaluation the next step in an analysis of particulate air quality in a region is a process that can be termed a descriptive air quality analysis. The objectives of a descriptive air quality analysis are: (1) to identify similarities and differences in air quality at different sampling sites; and (2) to depict temporal and spatial variations in particulate and gaseous precursor measurements. Descriptive air quality analysis includes: (1) statistical summaries of median and extreme values of air quality variables for different sites, episodes, and times of day; (2) time series plots of PM_{10} and selected chemical components; (3) spatial pie plots of particulate chemical composition; and (4) spatial and temporal correlations between PM_{10} and chemical composition measurements. The product of this analysis is a quantitative overview of particulate concentrations during the period of interest.

Performed at the same time as a descriptive air quality analysis, a descriptive meteorological analysis is carried out to: (1) describe the spatial structure, temporal variability, and statistical distribution of meteorological conditions; (2) describe the transport and mixing patterns in the study domain; and (3) identify relationships between meteorology and atmospheric particulate concentrations. Data normally available would include wind speed, wind direction, temperature, relative humidity, and solar radiation at ground level and aloft (if available).

Descriptive meteorological analysis activities include: (1) statistical summaries of meteorological variables; (2) time series and spatial plots of meteorological variables, including wind vectors, with examination for phenomena such as inter-basin transport, stagnation, slope flows, convergence zones, and recirculation; (3) identification of layers and orographic phenomena that change with elevation; (4) tabulations of fog occurrences,

frequencies, locations, and intensities; and (5) meteorological descriptions and comparisons with meteorology during high PM_{10} episodes from prior years.

The product of these analyses is a conceptual understanding of how meteorological phenomena influence atmospheric particulate concentrations in a particular region.

The next step in receptor modeling for particulate matter is a source profile compilation. The objectives of source profile compilation analysis are: (1) to combine profiles from individual samples into composite profiles; and (2) to assign source profiles to source categories based on their degree of similarity or difference. Data needed for this study are the chemical measurements on samples from representative source types that are expected to contribute to airborne particulate matter during study periods. Major source types include, for example: (1) suspended geological material from roads and from agricultural and unpaved areas; (2) primary particle exhaust from gasoline- and diesel-powered vehicles; (3) industrial sources; (4) residual oil combustion; and (5) secondary ammonium sulfate and ammonium nitrate originating from gaseous precursors. Source profile compilations include: (1) tables and plots of individual profiles and their uncertainties; (2) calculation of averages and standard deviations for category profiles; and (3) calculation of weighted composite profiles for source categories which are found for the source apportionment modeling described below. It is important to emphasize that source and ambient samples must be analyzed using the same protocols and methods (U.S. Environmental Protection Agency, 1994).

The chemical mass balance (CMB) receptor model is the model most commonly used for particulate matter source apportionment. The CMB model uses the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of, and quantify source contributions to, the receptor (Friedlander, 1973).

The CMB consists of an effective variance least-squares solution to the set of linear equations (5-4) that expresses each concentration of a chemical species at a receptor site as a linear sum of products of source profile species and source contributions. The source profile species, i.e., the fractional amount of the species in the emissions from each source type, and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the CMB model. The output consists of: (1) the source contribution estimates of

each source type; (2) the standard errors of these source contribution estimates; and (3) the amount contributed by each source type to each chemical species. The model calculates values for the contributions from each source type and the uncertainties associated with those values. Input data uncertainties are used both to weight the importance of input data values in the solution and to calculate the uncertainties of the source contributions. The CMB model assumptions are: (1) compositions of source emissions are constant over the period of ambient and source sampling; (2) chemical species do not react with each other, i.e., they add linearly; (3) all sources with a potential for significantly contributing to the receptor have been identified and their emissions have been characterized; (4) the source compositions are linearly independent of each other; (5) the number of sources or source categories is less than or equal to the number of chemical species; and (6) measurement uncertainties are random, uncorrelated, and normally distributed. Assumptions 1 through 6 for the CMB model are fairly restrictive and will never be completely satisfied in actual practice. Fortunately, the CMB model can tolerate reasonable deviations from these assumptions, although these deviations increase the stated uncertainties of the source contribution estimates.

The CMB modeling procedure requires: (1) identification of the contributing source types; (2) selection of chemical species to be included; (3) estimation of the fraction of each of the chemical species which is contained in each source type (i.e., the source compositions); (4) estimation of the uncertainty in both ambient concentrations (including artifacts during sampling and storage such as gas absorption or volatilization in filter samples) and source compositions; (5) estimation of differential losses during transport from source to receptor; (6) solution of the chemical mass balance equations; and (7) validation and reconciliation. Each of these steps requires different types of data. Uncertainties in the modeling results can be noticeably reduced by obtaining source profile measurements which correspond to the period of ambient measurements (Glover et al., 1991; Dzubay et al., 1988; and Olmez et al., 1988). Stratifying data according to wind direction can also increase the number of source types that can be resolved as shown in the above studies.

Emissions inventories are examined to determine the types of sources that are most likely to influence a receptor. These emissions inventories for particulate matter are

frequently far from complete, however, and other measures are needed to infer the influence of uninventoried sources. The Principal Components Analysis and Empirical Orthogonal Function models described below can aid in this identification. Once these sources have been identified, profiles acquired from similar sources can be examined to select the chemical species to be measured. The more species measured, the better the precision of the CMB apportionment.

The Principal Components Analysis (PCA) receptor model classifies variables into groups identifiable as causes of particulate matter levels measured at receptors. Typical causes are emissions sources, chemical interactions, or meteorological phenomena. The PCA model uses ambient concentrations of chemical species and meteorological data as inputs. PCA does not use source emissions measurements, as does the CMB model, but it may require 50 or more measurements of many species from different time periods at a single receptor site.

The PCA procedure is as follows: (1) select the chemical species and measurement cases to be included; (2) calculate the correlation coefficients between the species; (3) calculate the eigenvectors and eigenvalues of the correlation matrix; (4) select eigenvectors to be retained; (5) rotate these eigenvectors into a more physically meaningful space; and (6) interpret the rotated vectors as air pollution sources based on the chemical species with which they are highly correlated. Freeman et al. (1989) describe the computer software and methods required to use the PCA model for PM_{10} source assessment. See also Henry (1991).

The PCA model assumptions are: (1) compositions of source emissions are constant over the period of ambient and source sampling; (2) chemical species concentrations add linearly; (3) measurement errors are random and uncorrelated; (4) the case-to-case variability of actual source contributions is much larger than the variability due to other causes, such as measurement uncertainty or changes in source profiles due to process and fuel changes; (5) causes of variability that affect all sources equally (such as atmospheric dispersion) have much smaller effects than causes of variability for individual source types (such as wind direction or emission rate changes); (6) the number of cases exceeds the number of variables in the PCA model to an extent that statistical stability is achieved; and (7) eigenvector rotations are physically meaningful.

There are a number of examples of the application of PCA models. Photochemical factors were found to influence particulate matter measurements from Los Angeles, CA, New York, NY (Henry and Hidy, 1979), St. Louis, MO (Henry and Hidy, 1982), Lewisburg, WV (Lioy et al., 1982), and Detroit, MI (Wolff et al., 1985a). These photochemical factors were consistently associated with daily average and maximum ozone (O_3), maximum temperatures, and absolute humidity. The photochemical factors found for Los Angeles data (Henry and Hidy, 1979) were highly correlated with daily maximum and minimum relative humidity measurements. Local source factors were found for Salt Lake City (Henry and Hidy, 1982) and Los Angeles (Henry and Hidy, 1979) and were highly correlated with sulfur dioxide (SO_2) and the wind direction frequency distributions. Dispersion/stagnation factors were found for St. Louis, Salt Lake City, and Lewisburg. The variables correlated with the dispersion/stagnation factor were nitric oxide (NO), nitrogen dioxide (NO_2), wind speed at midnight and noon, average wind speed, morning mixing height, maximum hourly precipitation, and average precipitation. PCA has also been used to identify sources which may not be inventoried (Wolff and Korsog, 1985; Cheng et al., 1988; Henry and Kim, 1989; Koutrakis and Spengler, 1987; Zeng and Hopke, 1989).

The PCA procedure as outlined above provides only a qualitative assessment of air pollution sources. In some circumstances, however, the procedure can be extended to produce quantitative estimates of the source impacts. For example, a chemical species strongly associated with a single PCA group may be suitable as a source tracer for use in a subsequent multiple linear regression receptor model (Kleinman et al., 1980)

The Empirical Orthogonal Function (EOF) receptor model is applied to a spatially dense network of measurements to identify the locations of emissions sources and to estimate the net fluxes (emissions minus deposition) of those pollutants. The EOFs manifest themselves as isopleth maps of flux density. When a major point source is the emitter, such as a coal-fired power plant, the EOFs have been shown (Gebhardt et al., 1990) to surround that source. EOFs have been applied to air pollution measurements by Peterson (1970), Ashbaugh et al. (1984), Wolff et al. (1985b), and Henry et al. (1990). Henry et al. (1990) were the first researchers to place this method on a firm theoretical foundation and to demonstrate that EOFs reproduce the net fluxes used as input to a dispersion model.

In prior studies, the EOF model was applied to single chemical constituents, such as sulfur dioxide, sulfate, and total particulate mass concentrations. In a recent study (Watson et al., 1991), the EOF model was applied to the source contribution estimates calculated for each sample from the CMB modeling described above. In this way, source-type specific patterns of net flux were determined. For example, the geological source contributions may be represented as a linear sum of EOFs which correspond to a dirt road, a construction site, and an area of intense agricultural activity. The motor vehicle exhaust source contributions may be represented by a linear sum of EOFs which correspond to a major highway, a large truck stop, or an urban core area. The EOF model may also be applied to specific chemical species which are identified as potential markers for uninventoried sources.

The EOF procedure is similar to the PCA procedure: (1) select the source contribution estimates and measurement cases to be included; (2) calculate the covariance coefficients between the species measured at the same time at several sites; (3) calculate the eigenvectors and eigenvalues of the covariance matrix; (4) select eigenvectors to be retained; (5) rotate these eigenvectors into a more physically meaningful space; and (6) interpolate between the values of these eigenvectors to supply the net flux patterns. The main difference between PCA and EOF is that PCA operates on many samples from a single site taken over an extended time period, while EOF operates on many samples from many sites taken over a single time period.

The formulation of Henry et al. (1990), termed Source Identification Through Empirical Orthogonal Functions (SITEOF), uses wind velocities as input in addition to the spatially distributed source contribution estimates. The SITEOF assumptions are: (1) net fluxes of spatially-distributed pollutants add linearly; (2) pollutants are homogeneously distributed vertically in the mixed layer; (3) measurement errors are random and uncorrelated; (4) the number of sampling sites exceeds the number of source locations to an extent that statistical stability is achieved; and (5) measurement locations are located in positions to maximize spatial gradients from major source emissions. The major unknown concerning the SITEOF model is the extent to which assumptions 4 and 5 can be met in actual practice. Motor vehicle exhaust is confined to specific areas (e.g., roads and parking lots), and it is a straightforward task to locate monitors close to and far from these known locations. Fugitive dust, on the other hand, can be emitted from many locations.

The SITEOF model is one of a class of procedures referred to as "hybrid receptor models". Such models make use of not only the ambient species concentration measurements that form the input data for a pure receptor model, but in addition source emission rates or atmospheric dispersion or transformation information characteristic of dispersion models. By exploiting simultaneously the strengths of the two complementary approaches their individual weaknesses should be minimized. A survey of hybrid receptor models is available (Lewis and Stevens, 1987).

Ashbaugh et al., (1985) developed the concept of the potential source contribution function (PSCF) for performing the apportionment of secondary species, for combining air parcel back trajectories from a receptor site with chemical data at the site to infer possible source locations. The PSCF is an estimate of the conditional probability that a trajectory which passed through a given cell in the emissions grid (g_{ij}) contributed a concentration greater than some threshold value to ambient concentrations at the receptor site. Gao et al. (1993) extended the PSCF analysis to provide an apportionment of secondary species. By multiplying the PSCF by the emissions rate in g_{ij}, an estimate of the maximum contribution of sources in g_{ij} to the concentrations measured at the receptor site is obtained. Further research is needed to quantify the uncertainties associated with this method. These uncertainties are related to unidentified sources, background sources, emissions estimates at the time of calculation, the differential loss of species (e.g., by deposition), and mixing of air parcels from different cells during transit from source to receptor. Gao et al. (1993) have applied PSCF's along with emissions estimates to the apportionment of SO_2 and $SO_4^=$ at sites in the South Coast Air Basin, and Cheng et al. (1996) have also applied this technique to the apportionment of NO_x and NH_3 in this area.

The use of ^{14}C isotopic analysis has been used to distinguish between fossil fuel and biomass sources of carbon in aerosol samples. An example would be to determine the fraction of ambient aerosol mass concentration in wintertime samples originating from woodburning. This method has been particularly useful in validating less expensive receptor methods of achieving the same goal (Wolff et al., 1981; Lewis et al., 1988).

The preceding sections have dealt with receptor models that rely on chemical information obtained from bulk samples. It is worth noting that in addition there are powerful receptor modeling methods which also use the morphology and composition of

individual particles to provide clues to their source origin (Dzubay and Mamane, 1989). Scanning electron microscopy (SEM) along with energy dispersive X-ray analysis (EDX) has allowed the size distribution of particles to be characterized according to shape and elemental composition. This technique has proven to be extremely useful for distinguishing between fly ash and soil derived particles; both types of particles have similar composition, but fly ash particles are spherical while soil particles are irregularly shaped.

Manually performing SEM/EDX analyses of the large number individual particles necessary to characterize a size distribution is extremely time consuming. Automated methods have been developed for the rapid characterization of the shapes of hundreds of particles in aerosol samples (Xie et al., 1994a, 1994b). The morphology data can then be used along with EDX data to assign particles to clusters related to specific source types (Van Espen, 1984).

5.5.3 Source Contributions to Ambient Particles Derived by Receptor Models

Receptor modeling has been used for obtaining information about the nature of sources of ambient aerosol samples. The results of several studies will be discussed to provide an indication of different sources of particulate matter across the United States. First, results obtained by using the CMB approach for estimating contributions to $PM_{2.5}$ and $PM_{(10-2.5)}$ from different source categories at monitoring sites in the United States east of the Mississippi River will be discussed. Estimated contributions from a number of source categories to PM_{10} in ambient samples, obtained mainly at sites west of the Mississippi River, will then be discussed.

Dzubay et al. (1988) estimated source category contributions to 24-hour $PM_{2.5}$ and $PM_{(10-2.5)}$ samples obtained by a dichotomous sampler at three widely separated sites in the Philadelphia, PA area (NE airport in Philadelphia, PA; Camden, NJ; and a site about 30 km to the SW of Camden, NJ) during the summer of 1982. They used a composite of CMB, multiple linear regression (MLR), and wind trajectory receptor models. Source compositions shown in Table 5-3 were obtained partly to provide input to this study (Olmez et al., 1988). Ambient concentrations of individual species used by Dzubay et al. (1988) are shown in Table 6A-2a (Chapter 6, Appendix A). Sulfate, associated NH_4+ and water

constituted about 70% of $PM_{2.5}$. Since the mean fractional abundances of $PM_{2.5}$ to PM_{10} was 0.75, it can be seen that sulfate components contributed approximately 53% of PM_{10}. Coal- and oil-fired power plants located east of the Mississippi River were found to contribute $50 \pm 6\%$ and $11 \pm 4\%$ of $PM_{2.5}$, by using Se as a tracer for coal combustion and V and Ni as tracers for oil combustion, based on an MLR analysis.

The study was performed during a period (summer of 1982) when the Pb content of gasoline was declining markedly, and so Pb could not be used as a unique tracer of motor vehicle emissions. CMB was used to determine nonvehicular Pb, which was subtracted from the measured Pb concentration to yield a tracer for vehicle exhaust. Motor vehicle exhaust was then found to contribute about 8%, on average, to $PM_{2.5}$. Local sources of sulfate (determined from the MLR intercept) were found to contribute 13%, on average, with smaller contributions from local industrial sources, incinerators, and crustal matter to $PM_{2.5}$.

Crustal matter constituted about 76%, on average, of $PM_{(10-2.5)}$. Sulfate and associated NH_4^+ and water constituted only about 7% of $PM_{(10-2.5)}$. Other contributions to $PM_{(10-2.5)}$ were found to arise from sea-salt and incinerators. In a study of the Philadelphia aerosol in the summer of 1994, Pinto et al. (1995) found close agreement with Dzubay et al. (1988) both in measured concentrations and in the magnitude of the inferred fractional contribution of regional sulfate sources.

Glover et al. (1991) estimated the contributions of different source categories to 24-hour $PM_{2.5}$ and $PM_{(10-2.5)}$ samples obtained with a dichotomous sampler at a site in Granite City, IL. Again, sulfate was the major constituent of $PM_{2.5}$, constituting from 59% of $PM_{2.5}$ with SSW winds to 86.6% of $PM_{2.5}$ with NNW winds. Inferred contributions from specific source types were also shown to be strongly dependent on wind direction. Inferred contributions from iron works ranged from 3.4% with NNW winds to 16.4% with SSE winds. Inferred contributions from a Pb smelter ranged from 2.8% with WNW winds to 11.6% with SSW winds. Inferred contributions from other sources (e.g., motor vehicles, incinerators, other smelters, and soil) were all typically a few per cent.

Sulfate was a relatively minor constituent (< 10%) of $PM_{(10-2.5)}$ samples. Major inferred contributions were from iron works, ranging from 5.7% with WNW winds to 53.8% with ENE winds; soil, ranging from 4.2% with WSW winds to 35.8% with ESE

winds; street dust, ranging from 1.4% SSE winds to 45.6% with WNW winds; with generally smaller contributions from the other sources listed for $PM_{2.5}$.

These results demonstrate the different nature of $PM_{2.5}$ and $PM_{(10-2.5)}$ sources (i.e., $PM_{2.5}$ was derived from regional sources, while $PM_{(10-2.5)}$ was derived from local industries); the utility of wind sectoring to help locate sources; and the need to obtain site-specific source composition profiles. The use of site-specific source profiles instead of profiles culled from the literature resulted in decreases in predicted error values, especially for fugitive dust.

Results obtained at a number of monitoring sites in the central and western United States obtained by using the CMB model are shown in Table 5-12 for PM_{10}. The sampling sites represent a variety of different source characteristics within different regions of Arizona, California, Colorado, Idaho, Illinois, Nevada and Ohio. Several of these are background sites, specifically Estrella Park, Gunnery Range, Pinnacle Peak, and Corona de Tucson, AZ, and San Nicolas Island, CA. Definitions of source categories also vary from study to study. In spite of these differences, several features can be observed from the values in this table.

Fugitive dust (geological material) from roads, agriculture and erosion appears as a highly variable contributor to PM_{10} at nearly all sampling sites shown in Table 5-12, contributing about 40% of the average PM_{10} mass concentration. The average fugitive dust source contribution is highly variable among sampling sites within the same urban areas, as seen by differences between the Central Phoenix (33 $\mu g/m^3$) and Scottsdale (25 $\mu g/m^3$) sites in Arizona, and it is also seasonally variable, as evidenced by the summer and fall contributions at Rubidoux, CA. These studies found that the source profiles for fugitive dust were chemically similar, even though the dust came from different emitters, so that further apportionment into sub-categories was not possible by the CMB model alone. Road sand often contains salts that allow it to be distinguished from other fugitive dust sources. It is usually the only exposed fugitive dust source when other sources are covered by snowpack. Dust from some construction activities and cement plants can also be separated from other sources due to enrichments in calcium content of these emissions, as seen in studies at Rubidoux, CA, Rillito, AZ (near cement plants), and Pocatello, ID (near chemical and fertilizer production plants).

TABLE 5-12. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

Sampling Site	Time Period	$\mu g/m^3$ Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Measured PM_{10} Concentration
Central Phoenix, AZ (Chow et al., 1991)	Winter 1989-1990	33.0	0.0	25.0	2.3	0.2	2.8	0.0	0.0	0.0	0.0	64.0
Craycroft, AZ (Chow et al., 1992a)	Winter 1989-1990	13.0	0.0	8.3	0.0	0.7	0.6	1.2	0.0	0.0	0.0	23.4
Hayden 1, AZ (Garfield) (Ryan et al., 1988)	1986	5.0	2.0	0.0	0.0	4.0	0.0	74.0	5.0[d]	1.0[e]	0.0	105.0
Hayden 2, AZ (Jail) (Ryan et al., 1988)	1986	21.0	4.0	0.0	0.0	4.0	0.0	28.0	0.0	1.0[e]	0.0	59.0
Phoenix, AZ (Estrella Park) (Chow et al., 1991)	Winter 1989-1990	37.0	0.0	10.0	0.9	1.6	0.0	0.0	0.0	0.0	0.0	55.0
Phoenix, AZ (Gunnery Rg.) (Chow et al., 1991)	Winter 1989-1990	20.0	0.0	5.5	0.0	1.0	0.0	0.0	0.0	0.0	0.0	27.0
Phoenix, AX (Pinnacle Pk.) (Chow et al., 1991)	Winter 1989-1990	7.0	0.0	2.9	1.0	0.9	0.0	0.0	0.0	0.0	0.0	12.0
Rillito, AZ (Thanukos et al., 1992)	1988	42.7	13.8	1.2[f]	0.0	0.0	0.0	11.6	0.0	0.0	0.0	79.5[g]
Scottsdale, AZ (Chow et al., 1991)	Winter 1989-1990	25.0	0.0	19.0	7.4	0.6	3.6	0.0	0.0	0.0	0.0	55.0
West Phoenix, AZ (Chow et al., 1991)	Winter 1989-1990	30.0	0.0	25.0	10.0	0.4	3.1	0.0	0.0	0.0	0.0	69.0
Bakersfield, CA (Magliano, 1988)	1986	27.4	3.0	5.5	9.6	5.6	0.0	0.5	0.0	0.0	0.0[j]	67.6
Bakerfield, CA (Chow et al., 1992b)	1988-1989	42.9	1.6	7.7	6.5	5.5	12.7	1.0	1.5[n]	0.6[k]	0.0	79.6
Crows Landing, CA (Chow et al., 1992b)	1988-1989	32.2	0.0	2.2	3.4	2.8	6.5	0.5	1.5[n]	1.2[k]	0.0	52.5
Fellows, CA (Chow et al., 1992b)	1988-1989	29.0	1.4	2.1	3.4	5.1	7.5	7.0	1.4[n]	1.4[k]	0.0	54.6
Fresno, CA (Magliano, 1988)	1986	17.1	0.7	4.0	9.2	1.8	0.0	0.1	0.0	0.0	0.0[j]	48.1
Fresno, CA (Chow et al., 1992b)	1988-1989	31.8	0.0	6.8	5.1	3.6	10.4	0.3	1.0[n]	0.1[k]	0.0	71.5
Indio, CA (Kim et al., 1992)		33.0	3.0	4.4	7.1	3.6	4.1	0.2	1.0[h]	0.0	0.0	58.0
Kern Wildlife Refuge, CA (Chow et al., 1992b)	1988-1989	15.1	2.0	2.2	4.0	3.3	1.5	0.5	1.5[n]	0.7[k]	0.0	47.8
Long Beach, CA (Gray et al., 1988)	1986	20.7	0.0	5.1	0.0	8.0	9.2	0.1	2.0[h]	6.4[k]	0.0	51.9[j]
Long Beach, CA (Summer) (Watson et al., 1994b)	Summer 1987	11.1	0.0	6.3	0.0	10.9	0.8	0.1	2.2[h]	0.0	0.0	46.1
Long Beach, CA (Fall) (Watson et al., 1994b)	Fall 1987	11.3	0.0	42.8	0.0	3.8	23.2	0.0	2.7[h]	0.0	0.0	96.1
Riverside, CA (Chow et al., 1992c)	1988	32.6	0.0	7.0	0.0	4.8	21.4	0.3	1.3[h]	1.1[o]	0.0	64.0
Rubidoux, CA (Gray et al., 1988)	1986	43.1	4.0	5.6[i]	0.0	6.4	21.3	0.3	1.0[h]	5.9[k]	0.0	87.4[j]
Rubidoux, CA (Summer) (Watson et al., 1994b)	Summer 1987	34.9	4.5	17.3	0.0	9.5	27.4	0.0	5.1[h]	0.0	0.0	114.8
Rubidoux, CA (Fall) (Watson et al., 1994b)	Fall 1987	19.2	16.1	30.3	0.0	2.1	31.6	0.0	1.1[h]	0.0	0.0	112.0
Rubidoux, CA (Chow et al., 1992c)	1988	48.0	0.0	10.2	0.0	5.3	21.7	0.4	1.5[h]	5.7[o]	0.0	87.0
San Nicolas Island, CA (Summer) (Watson et al., 1994b)	Summer 1987	1.6	0.0	0.9	0.0	3.7	0.5	0.0	4.3[h]	0.0	0.0	17.4

TABLE 5-12 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM$_{10}$

Sampling Site	Time Period	Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Measured PM$_{10}$ Concentration
Stockton, CA (Chow et al., 1992b)	1989	34.4	0.5	5.2	4.8	3.1	7.0	0.7	1.8[n]	0.0[k]	0.0	62.4
Pocatello, ID (Houck et al., 1992)	1990	8.3	7.5	0.1	0.0	0.0	0.0	0.0	0.0	84.1	0.0	100.0
S. Chicago, IL (Hopke et al., 1988)	1986	27.2	2.4	2.8	0.0	15.4	--	15.1	2.2[u]	0.0	0.0	80.1
S.E. Chicago, IL (Vermette et al., 1992)	1988	14.7	0.0	0.9	[f]0.0	7.7	--	0.8	0.3[h]	1.1[w]	7.7[g]	41.0[t]
Reno, NV (Chow et al., 1988)	1986-1987	14.9	0.0	10.0	1.9	1.3	0.6	0.0	0.0	0.0	0.0	30.0
Sparks, NV (Chow et al., 1988)	1986-1987	15.1	0.0	11.6	13.4	2.7	0.9	0.0	0.0	0.2	0.0	41.0
Follansbee, WV (Skidmore et al., 1992)	1991	10.0	0.0	35.0	0.0	16.0	--	9.3	0.0	0.0	0.0	66.0
Mingo, OH (Skidmore et al., 1992)	1991	12.0	0.0	14.0	4.1	15.0	--	3.4	11.0[x]	0.0	0.0	60.0
Steubenville, OH (Skidmore et al., 1992)	1991	8.3	0.0	14.0	0.8	14.0	--	3.8	5.0[x]	0.0	0.0	46.0

[a] Smelter background aerosol.
[b] Cement plant sources, including kiln stacks, gypsum pile, and kiln area.
[c] Copper ore.
[d] Copper tailings.
[e] Copper smelter building.
[f] Heavy-duty diesel exhaust emission.
[g] Background aerosol.
[h] Marine aerosol, road salt, and sea salt plus sodium nitrate.
[i] Motor vehicle exhaust from diesel and leaded gasoline.

Residual oil combustion.
Secondary organic carbon.
Biomass burning.
Primary crude oil.
NaCl + NaNO$_3$.
Lime.
Road sanding material.
Asphalt industry.
Phosphorus/phosphate industry.

Regional sulfate.
Steel mills.
Refuse incinerator.
Local road dust, coal yard road dust, steel haul road dust.
Incineration.
Unexplained mass.

Dust sources constitute 88% of the annual average PM_{10} National Emissions Inventory (U.S. Environmental Protection Agency, 1994), but they average more than 50% of the contribution to average PM_{10} concentrations in only about 40% of the entries shown in Table 5-12. The reasons for this apparent discrepancy are not clear. In addition to errors in inventories or source apportionments, weather-related factors (wind speed and ground wetness) and the dominance of local sources on spatial scales too small to be captured in inventories may be involved. It should be remembered that dust emissions are widely dispersed and highly sporadic. Dust particles also have short atmospheric residence times and as a result their dominance in emissions inventories may not be reflected in samples collected near specific sources. The contributions from primary motor vehicle exhaust, residential wood combustion, and industrial sources would be underestimated if values from the National Emissions Inventory Trends data base (U.S. Environmental Protection Agency, 1994) were used. Some of these deficiencies, such as fugitive dust emissions, are probably intractable, and the best that can be done is to estimate the uncertainties in these emissions and to value the data accordingly when decisions are made.

In Table 5-12, primary motor vehicle exhaust contributions account for up to 40% of average PM_{10} at many of the sampling sites. Vehicle exhaust contributions are also variable at different sites within the same study area. The mean value and the variability of motor vehicle exhaust contributions reflects the proximity of sampling sites to roadways and traffic conditions during the time of sampling. Vegetation burning, which includes agricultural fires, wildfires, prescribed burning, and residential wood combustion, was found to be significant at residential sampling sites such as: Craycroft, Scottsdale, and West Phoenix, AZ; Fresno, Bakersfield, and Stockton, CA; Sparks, NV; and Mingo, OH. The predominance of these contributions during winter months and the local rather than regional coverage indicates that residential wood combustion was the major sub-category, even though chemical profiles are too similar to separate residential combustion from other vegetative burning sources. For example, Chow et al. (1988) show substantial differences between the residential Sparks, NV and urban-commercial Reno, NV burning contributions even though these sites are separated by less than 10 km. Sites near documented industrial activity show evidence of that activity, but not necessarily involving primary particles emitted by point sources. Hayden, AZ, for example, contains a large smelter, but the major smelter contributions appear to arise from fugitive

emissions of copper tailings rather than stack emissions. Secondary sulfate contributions at Hayden were low, even though SO_2 emissions from the stack were substantial during the time of the study. Fellows, CA is in the midst of oilfield facilities that burn crude oil for tertiary oil extraction. These have been converted to natural gas since the 1988 to 1989 study period. The Follansbee, WV, Mingo, OH, and Steubenville, OH sites are all close to each other in the Ohio River Valley and show evidence of the widespread steel mill emissions in that area.

Marine aerosol is found, as expected, at coastal sites such as Long Beach (average 3.8% of total mass), and San Nicolas Island (25%). These contributions are relatively variable and are larger at the more remote sites. Individual values reflect proximity to local sources. Of great importance are the contributions from secondary ammonium sulfate and ammonium nitrate in the western United States. These are especially noticeable at sites in California's San Joaquin Valley (Bakersfield, Crows Landing, Fellows, Fresno, Kern Wildlife, and Stockton) and in the Los Angeles area.

In addition to these commonly measured components, it is possible that isotopic ratios in source emissions may vary in an informative way with the nature of the combustion process and with the geologic age and character of the source input material. Carbon-14, for example, has been used to separate contemporary carbon due to vegetative burning from carbon emitted by fossil fuel combustion (Currie et al., 1984). Organic compounds (Rogge et al., 1991, 1993a, 1993b, 1993c, 1993d, 1993e; Lowenthal et al., 1994; Hildemann et al., 1991, 1993) show great promise for further differentiation among sources, but measurement methods need to be standardized and made more cost-effective to take advantage of extended chemical source profiles.

Several aspects of the data in Table 5-12 limit the generalizations that can be drawn from it:

- The source contribution estimates for the receptor sites shown are for different years and different times of year. The results, therefore, do not show the temporal variability which may exist in relative source contributions and should not be used to infer differences between sites.

- Samples selected for chemical analysis are often biased toward the highest PM_{10} mass concentrations in these studies, so average source contribution estimates are probably not representative of annual averages.

- Many studies were conducted during the late 1980s, when a portion of the vehicle fleet still used leaded gasoline. While the lead and bromine in motor vehicle emissions facilitated the distinction of motor vehicle contributions from other sources, it was also associated with higher emission rates than vehicles using unleaded fuels. Lead has been virtually eliminated from vehicle fuels.

- Uncertainties of source contribution estimates are not usually reported with the average values summarized in Table 5-12. Estimates of standard errors are calculated in source apportionment studies, and typically range from 15 to 30% of the source contribution estimate. They are much higher when the chemical source profiles for different sources are highly uncertain or too similar to distinguish one source from another.

- Different measurement sites within the same airshed show different proportions of contributions from the same sources. Most often, the sites in close proximity to an emitter show a much larger contribution from that emitter than sites that are distant from that emitter, even by distances as short as 10 km (e.g., Chow et al., 1988; 1992c).

- Given the mass, trace element, ion, and carbon components measured in source and receptor samples in most of the studies from Table 5-12, greater differentiation among sources (e.g., diesel and gasoline vehicle exhaust, meat cooking and other organic carbon sources, different sources of fugitive dust, and secondary aerosol precursors) is not possible for the studies shown in Table 5-12.

5.6   SUMMARY AND CONCLUSIONS

Ambient particulate matter contains both primary and secondary components. Due to the complexity of the composition of ambient PM_{10}, sources are best discussed in terms of individual constituents of both primary and secondary PM_{10}. Each of these constituents can have anthropogenic and natural sources, as shown in Tables 5-1A and 5-1B. The distinction between natural and anthropogenic sources is not always obvious. While windblown dust might seem to be the result of natural processes, highest emission rates are associated with agricultural activities in areas that are susceptible to periodic drought. Examples include the dust bowl region of the midwestern United States and the Sahel of Africa. Most forest fires in the United States may ultimately be of human origin, either through prescribed burning or accident.

Windblown dust from whatever source represents the largest single source of PM in U.S. and global emissions inventories. Although dust emissions (88% of total U.S. PM_{10})

are far in excess of any other source of primary or secondary PM_{10} in any region of the country, measurements of soil constituents in ambient samples suggest that the overall contribution from this source could be much lower. The reasons for this apparent discrepancy are not clear. In addition to errors in inventories or source apportionments, weather-related factors (wind speed and ground wetness) and the dominance of local sources on spatial scales too small to be captured in inventories may be involved. It should be remembered that dust emissions are widely dispersed and highly sporadic. Dust particles also have short atmospheric residence times and, as a result, their dominance in emissions inventories may not be reflected in samples collected near specific sources.

There is a great deal of spatial and temporal variability which is still not reflected in emissions inventories. Apart from seasonal variability, many of the sources discussed in this chapter are highly episodic even within their peak emissions seasons. Examples include the long-range transport of Saharan dust to the United States, regional dust storms, volcanism, and forest fires. Their spatial variability is also evident. Annual estimates for an area can easily be exceeded in a few days by unusual events involving these sources. Less dramatic examples of strong seasonal variability, such as wood burned for home heating in the northwestern United States, may be the major source of winter PM there.

It might be thought that enough data are available to adequately characterize mobile and stationary source emissions. However, data characterizing the variability of PM emissions from mobile sources are quite sparse. Available data suggest that elemental carbon followed by organic carbon species are the major components of diesel particulate emissions, while organic carbon emissions are larger than elemental carbon emissions in the case of gasoline fueled vehicles.

Emissions from biomass burning are also composed mainly of organic carbon species and elemental carbon, although the ratio of organic carbon to elemental carbon is much higher than in motor vehicle emissions. Power plant emissions are not significant sources of aerosol carbon. The fractional yield of secondary organic carbon from the oxidation of natural and anthropogenic hydrocarbons is highly uncertain. Yields from the oxidation of anthropogenic hydrocarbons are probably less than a few percent, and larger yields are found in the oxidation of terpenes emitted by vegetation.

As seen in Table 5-1B, emissions of surface dust, organic debris, and sea spray are concentrated mainly in the coarse fraction of PM_{10} (> 2.5 µm aero. diam.). A small fraction of this material is in the $PM_{2.5}$ size range (< 2.5 µm aero. diam., c.f. Figure 5-1). Nevertheless, concentrations of crustal material can be appreciable especially during dust events. It should also be remembered that all of the Saharan dust reaching the United States is in the $PM_{2.5}$ size range. Emissions from combustion sources (mobile and stationary sources, biomass burning) are predominantly in the $PM_{2.5}$ size range.

As shown in Table 5-6, estimated primary PM_{10} emissions decreased by about 10% from 1985 through 1993. A high degree of variability is evident for emissions from miscellaneous (fugitive dust, biomass burning, and agriculture) and natural (wind erosion of natural surfaces) categories shown in Table 5-7. Estimated SO_2 emissions decreased by several per cent from 1984 through 1993 as shown in Table 5-8. Estimated emissions of NO_x show little variation over the same time period as shown in Table 5-9. Emissions of primary PM_{10} are projected to increase to the year 2010 mainly because of increases in fugitive dust emissions, while emissions of SO_2 and NO_x are expected to decrease over the same time period.

Uncertainties in emissions inventories are difficult to quantify. They may be as low as 10% for well-defined sources (e.g., for SO_2) and may range up to a factor of 10 or so for windblown dust. As a rule, total PM emissions rates should be regarded as order-of-magnitude estimates. Because of the large uncertainty associated with emissions of suspended dust, trends of total PM_{10} emissions should be viewed with caution and emissions from specific source categories are best discussed on an individual basis.

Emissions inventories are generally not the most appropriate way to apportion material in ambient samples. Receptor modeling has proven to be an especially valuable tool in this regard. Compositional profiles developed for receptor modeling applications are perhaps the most accessible and reliable means to characterize the composition of emissions. Quoted uncertainties in source apportionments of constituents in ambient aerosol samples typically range from 15 to 30%. Receptor modeling studies in the western United States have found that motor vehicles and fugitive dust are major sources of PM_{10}. Likewise, a limited number of studies in the eastern United States have found that fossil fuel combustion and fugitive dust are major sources of PM_{10}. Techniques are currently being developed to use receptor

modeling techniques along with ambient data to refine emissions inventory estimates. Because of the site-specific nature of receptor modeling results, more rigorous methods for determining site locations and methods for applying receptor model results to larger spatial scales are needed for this purpose. Again, it should be emphasized that, because of limitations in receptor modeling methods in treating secondary components, these efforts are more likely to be successful for primary components, although it should be mentioned that methods are being developed to apportion secondary constituents.

REFERENCES

Alfaro, S. C.; Gomes, L. (1995) Improving the large-scale modeling of the saltation flux of soil particles in presence of nonerodible elements. J. Geophys. Res. [Atmos.] 100: 16,357-16,366.

Altshuller, A. P. (1983) Review: natural volatile organic substances and their effect on air quality in the United States. Atmos. Environ. 17: 2131-2165.

Altshuller, A. P.; Bufalini, J. J. (1965) Photochemical aspects of air pollution: a review. Photochem. Photobiol. 4: 97-146.

Andreae, M. O. (1991) Biomass burning: its history, use, and distribution and its impact on environmental quality and global climate. In: Levine, J. S., ed. Global biomass burning: atmospheric, climatic, and biospheric implications. Cambridge, MA: MIT Press; pp. 1-21.

Ashbaugh, L. L.; Myrup, L. O.; Flocchini, R. G. (1984) A principal component analysis of sulfur concentrations in the western United States. Atmos. Environ. 18: 783-791.

Ashbaugh, L. L.; Malm, W. C.; Sadeh, W. Z. (1985) A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. Atmos. Environ. 19: 1263-1270.

Bagnold, R. A. (1941) The physics of blown sand and desert dunes. London, United Kingdom: Methuen & Co.

Behymer, T. D.; Hites, R. A. (1984) Similarity of some organic compounds in spark-ignition and diesel engine particulate extracts. Environ. Sci. Technol. 18: 203-206.

Belly, P.-Y. (1964) Sand movement by wind. Washington, DC: U.S. Army Corps of Engineers, Coastal Engineering Research Center; technical memorandum no. 1.

Bisal, F.; Hsieh, J. (1966) Influence of moisture on erodibility of soil by wind. Soil Sci. 102: 143-146.

Brown, M. (1993) Deduction of emissions of source gases using an objective inversion algorithm and a chemical transport model. J. Geophys. Res. [Atmos.] 98: 12,639-12,660.

Calvert, J. G.; Heywood, J. B.; Sawyer, R. F.; Seinfeld, J. H. (1993) Achieving acceptable air quality: some reflections on controlling vehicle emissions. Science 261: 37-45.

Cheng, M.-D.; Lioy, P. J.; Opperman, A. J. (1988) Resolving PM 10 data collected in New Jersey by various multivariate analysis techniques. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 472-483. (APCA transactions series TR-13).

Cheng, M.-D.; Gao, N.; Hopke, P. K. (1996) Source apportionment study of nitrogen species measured in sourthern California in 1987. J. Environ. Eng. (N. Y.) 122: in press.

Chepil, W. S. (1945) Dynamics of wind erosion. Soil Sci. 60: 305-320.

Chepil, W. S. (1956) Influence of moisture on erodibility of soil by wind. Soil Sci. Soc. Am. Proc. 20: 288-292.

Chow, J. C.; Watson, J. G.; Frazier, C. A.; Egami, R. T.; Goodrich, A.; Ralph, C. (1988) Spatial and temporal source contributions to PM_{10} and $PM_{2.5}$ in Reno, NV. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 438-457. (APCA transactions series TR-13).

Chow, J. C.; Watson, J. G.; Richards, L. W.; Haase, D. L.; McDade, C.; Dietrich, D. L.; Moon, D.; Sloane, C. (1991) The 1989-90 Phoenix PM$_{10}$ study, v. II: source apportionment [final report]. Phoenix, AZ: Arizona Department of Environmental Quality; report no. 8931.6F1; Table 3-1.

Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Frazier, C. A.; Hinsvark, B. A.; Prichett, L. C.; Neuroth, G. R. (1992a) Wintertime PM$_{10}$ and PM$_{2.5}$ chemical compositions and source contributions in Tucson, Arizona. In: Chow, J. C.; Ono, D. M., eds. PM$_{10}$ standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. I; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 231-243. (A&WMA transactions series no. 22).

Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Solomon, P. A.; Magliano, K. L.; Ziman, S. D.; Richards, L. W. (1992b) PM10 source apportionment in California's San Joaquin Valley. Atmos. Environ. Part A 26: 3335-3354.

Chow, J. C.; Liu, C. S.; Cassmassi, J.; Watson, J. G.; Lu, Z.; Pritchett, L. C. (1992c) A neighborhood-scale study of PM$_{10}$ source contributions in Rubidoux, California. Atmos. Environ. Part A 26: 693-706.

Chow, J. C.; Watson, J. G.; Houck, J. E.; Pritchett, L. C.; Rogers, C. F.; Frazier, C. A.; Egami, R. T.; Ball, B. M. (1994) A laboratory resuspension chamber to measure fugitive dust size distributions and chemical compositions. Atmos. Environ. 28: 3463-3481.

Cofer, W. R.; Levine, J. S.; Sebacher, D. I.; Winstead, E. L.; Riggan, P. J.; Brass, J. A.; Ambrosia, V. G. (1988) J. Geophys. Res. [Atmos.] 93: 5207-5212.

Cooper, J. A.; Watson, J. G., Jr. (1980) Receptor oriented methods of air particulate source apportionment. J. Air Pollut. Control Assoc. 30: 1116-1125.

Cooper, J. A.; Redline, D. C.; Sherman, J. R.; Valdovinos, L. M.; Pollard, W. L.; Scavone, L. C.; Badgett-West, C. (1987) PM$_{10}$ source composition library for the South Coast Air Basin: volume I, source profile development documentation final report. El Monte, CA: South Coast Air Quality Management District; July 15.

Currie, L. D.; Gerlach, R. W.; Lewis, C. W.; Balfour, W. D.; Cooper, J. A.; Dattner, S. L.; De Cesar, R. T.; Gordon, G. E.; Heisler, S. L.; Hopke, P. K.; Shah, J. J.; Thurston, G. D.; Williamson, H. J. (1984) Interlaboratory comparison of source apportionment procedures: results for simulated data sets. Atmos. Environ. 18: 1517-1537.

Daisey, J. M.; Cheney, J. L.; Lioy, P. J. (1986) Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling. J. Air Pollut. Control Assoc. 36: 17-33.

Dasch, J. M. (1982) Particulate and gaseous emissions from wood-burning fireplaces. Environ. Sci. Technol. 16: 639-645.

Dattner, S. L.; Hopke, P. K. (1982) Receptor models applied to contemporary pollution problems: an introduction. In: Frederick, E. R., ed. A specialty conference on: receptor models applied to contemporary pollution problems; October; Danvers, MA. Pittsburgh, PA: Air Pollution Control Association; pp. 1-5. (APCA specialty conference proceedings SP-48).

Dentener, F. J.; Crutzen, P. J. (1994) A three-dimensional model of the global ammonia cycle. J. Atmos. Chem. 19: 331-369.

Dzubay, T. G.; Mamane, Y. (1989) Use of electron microscopy data in receptor models for PM-10. Atmos. Environ. 23: 467-476.

Dzubay, T. G.; Stevens, R. K.; Gordon, G. E.; Olmez, I.; Sheffield, A. E.; Courtney, W. J. (1988) A composite receptor method applied to Philadelphia aerosol. Environ. Sci. Technol. 22: 46-52.

Federal Register. (1977) Method 5 - determination of particulate emissions from stationary sources. F. R. (August 18) 42: 41776-41783.

Freeman, D. L.; Chow, J. C.; Egami, R. T.; Watson, J. G. (1989) A receptor and dispersion modeling software package. In: Watson, J. G., ed. Receptor models in air resources management: an international specialty conference; February 1988; San Francisco, CA. Pittsburgh, PA: Air & Waste Management Association; pp. 243-268. (APCA transactions series: no. 14).

Friedlander, S. K. (1973) Chemical element balances and identification of air pollution sources. Environ. Sci. Technol. 7: 235-240.

Fujita, E. M.; Croes, B. E.; Bennett, C. L.; Lawson, D. R.; Lurmann, F. W.; Main, H. H. (1992) Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's south coast air basin. J. Air Waste Manage. Assoc. 42: 264-276.

Gao, N.; Cheng, M.-D.; Hopke, P. K. (1993) Potential source contribution function analysis and source apportionment of sulfur species measured at Rubidoux, CA during the Southern California Air Quality Study, 1987. Anal. Chim. Acta 277: 369-380.

Gatz, D. F. (1995) A large silicon-aluminum aerosol plume in central Illinois: Saharan Desert dust? Atmos. Environ.: accepted.

Gebhart, K. A.; Lattimer, D. A.; Sisler, J. F. (1990) Empirical orthogonal function analysis of the particulate sulfate concentrations measured during WHITEX. In: Mathai, C. V., ed. Visibility and fine particles: an A&WMA/EPA international specialty conference; October 1989; Estes Park, CO. Pittsburgh, PA: Air & Waste Management Association; pp. 860-871. (A&WMA transactions series no. TR-17).

Geron, C. D.; Guenther, A. B.; Pierce, T. E. (1994) An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. J. Geophys. Res. [Atmos.] 99: 12,773-12,791.

Gillette, D. A.; Adams, J.; Endo, A.; Smith, D.; Kihl, R. (1980) Threshold velocities for input of soil particles into the air by desert soils. J. Geophys. Res. C: Oceans Atmos. 85: 5621-5630.

Gillette, D. A.; Adams, J.; Muhs, D. R.; Khil, R. (1982) Threshold friction velocities and rupture moduli for crusted desert soils for the input of soil particles into the air. J. Geophys. Res. B 87: 9003-9015.

Glover, D. M.; Hopke, P. K.; Vermette, S. J.; Landsberger, S.; D'Auben, D. R. (1991) Source apportionment with site specific source profiles. J. Air Waste Manage. Assoc. 41: 294-305.

Goklany, I. M.; Hoffnagle, G. F.; Brackbill, E. A. (1984) Acidic and total primary sulfates: development of emission factors for major stationary combustion sources. J. Air Pollut. Control Assoc. 34: 124-134.

Gordon, G. E. (1980) Receptor models. Environ. Sci. Technol. 14: 792-800.

Gordon, G. E. (1988) Receptor models. Environ. Sci. Technol. 22: 1132-1142.

Gray, H. A.; Landry, B.; Liu, C. S.; Henry, R. C.; Cooper, J. A.; Sherman, J. R. (1988) Receptor modeling for PM10 source apportionment in the South Coast Air Basin of California. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 399-418. (APCA transactions series TR-13).

Grosjean, D.; Seinfeld, J. H. (1989) Parameterization of the formation potential of secondary organic aerosols. Atmos. Environ. 23: 1733-1747.

Haagen-Smit, A. J. (1952) Chemistry and physiology of Los Angeles smog. Ind. Eng. Chem. 44: 1342-1346.

Hall, F. F., Jr. (1981) Visibility reductions from soil dust in the western U.S. In: White, W. H.; Moore, D. J.; Lodge, J. P., Jr., eds. Plumes and visibility: measurements and model components: proceedings of the symposium; November 1980; Grand Canyon National Park, AZ. Atmos. Environ. 15: 1929-1933.

Hammerle, R. H.; Korniski, T. J.; Weir, J. E.; Chladek, E.; Glerczak, C. A.; Chase, R. E.; Hurley, R. G. (1992) Effect of mileage accumulation on particulate emissions from vehicles using gasoline with methylcyclopentadienyl manganese tricarbonyl. Presented at: International congress & exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers; SAE technical paper no. 920731.

Hansen, A. D. A.; Rosen, H. (1990) Individual measurements of the emission factor of aerosol black carbon in automobile plumes. J. Air Waste Manage. Assoc. 40: 1654-1657.

Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H. (1989) Reactions of ozone with α-pinene and β-pinene in air: yields of gaseous and particulate products. J. Geophys. Res. [Atmos.] 94: 13,013-13,024.

Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H.; Washida, N. (1991) Reactions of OH with α-pinene and β-pinene in air: estimate of global CO production from the atmospheric oxidation of terpenes. J. Geophys. Res. [Atmos.] 96: 947-958.

Henry, R. C. (1991) Multivariate receptor models. In: Hopke, P. K., ed. Receptor modeling for air quality management. Amsterdam, The Netherlands: Elsevier; pp. 117-147.

Henry, R. C.; Hidy, G. M. (1979) Multivariate analysis of particulate sulfate and other air quality variables by principal components—part I: annual data from Los Angeles and New York. Atmos. Environ. 13: 1581-1596.

Henry, R. C.; Hidy, G. M. (1982) Multivariate analysis of particulate sulfate and other air quality variables by principal components—II: Salt Lake City, Utah and St. Louis, Missouri. Atmos. Environ. 16: 929-943.

Henry, R. C.; Kim, B. M. (1989) A factor analysis receptor model with explicit physical constraints. In: Watson, J. G., ed. Receptor models in air resources management: an international specialty conference; February 1988; San Francisco, CA. Pittsburgh, PA: Air & Waste Management Association; pp. 214-225. (APCA transactions series: no. 14).

Henry, R. C.; Wang, Y.-J.; Gebhart, K. A. (1990) The relationship between empirical orthogonal functions and sources of air pollution. Atmos. Environ. Part A 24: 503-509.

Hertel, O.; Christensen, J.; Hov, Ø, (1994) Modelling of the end products of the chemical decomposition of DMS in the marine boundary layer. Atmos. Environ. 28: 2431-2449.

Hildemann, L. M.; Markowski, G. R.; Jones, M. C.; Cass, G. R. (1991) Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. Aerosol Sci. Technol. 14: 138-152.

Hildemann, L. M.; Cass, G. R.; Mazurek, M. A.; Simoneit, B. R. T. (1993) Mathematical modeling of urban organic aerosol: properties measured by high-resolution gas chromatography. Environ. Sci. Technol. 27: 2045-2055.

Hooker, C. L.; Westberg, H. H.; Sheppard, J. C. (1985) Determination of carbon balances for smog chamber terpene oxidation experiments using a ^{14}C tracer technique. J. Atmos. Chem. 2: 307-320.

Hopke, P. K. (1985) Receptor modeling in environmental chemistry. New York, NY: John Wiley & Sons.

Hopke, P. K., ed. (1991) Receptor modeling for air quality management. New York, NY: Elsevier Science Publishing Company, Inc. (Vandeginste, B. G. M.; Kvalheim, O. M., eds. Data handling in science and technology: v. 7).

Hopke, P. K.; Lamb, R. E.; Natusch, D. F. S. (1980) Multielemental characterization of urban roadway dust. Environ. Sci. Technol. 14: 164-172.

Hopke, P. K.; Wlaschin, W.; Landsberger, S.; Sweet, C.; Vermette, S. J. (1988) The source apportionment of PM10 in south Chicago. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 484-494. (APCA transactions series TR-13).

Houck, J. E.; Chow, J. C.; Watson, J. G.; Simons, C. A.; Pritchett, L. C.; Goulet, J. M.; Frazier, C. A. (1989) Determination of particle size distribution and chemical composition of particulate matter from selected sources in California: volume I and executive summary (final report). Sacramento, CA: California Air Resources Board.

Houck, J. E.; Goulet, J. M.; Chow, J. C.; Watson, J. G.; Pritchett, L. C. (1990) Chemical characterization of emission sources contributing to light extinction. In: Mathai, C. V., ed. Visibility and fine particles: an A&WMA/EPA international specialty conference; October 1989; Estes Park, CO. Pittsburgh, PA: Air & Waste Management Association; pp. 437-446. (A&WMA transactions series no. TR-17).

Houck, J. E.; Rau, J. A.; Body, S.; Chow, J. C. (1992) Source apportionment: Pocatello, Idaho PM_{10} nonattainment area. In: Chow, J. C.; Ono, D. M., eds. PM_{10} standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. I; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 219-230. (A&WMA transactions series no. 22).

Huang, X.; Olmez, I.; Aras, N. K.; Gordon, G. E. (1994) Emissions of trace elements from motor vehicles: potential marker elements and source composition profile. Atmos. Environ. 28: 1385-1391.

Ingalls, M. N. (1989) On-road vehicle emission factors from measurements in a Los Angeles area tunnel. Presented at: 82nd annual meeting & exhibition of the Air and Waste Management Association; June; Anaheim, CA. Pittsburgh, PA: Air and Waste Management Association; paper no. 89-137.3.

Intergovernmental Panel on Climate Change. (1995) Climate change 1995: the science of climate change: draft summary for policymakers (SPM) of the draft contribution of Working Group I to the IPCC second assessment report. Geneva, Switzerland: World Meteorological Association, IPCC Secretariat; November.

Izumi, K.; Fukuyama, T. (1990) Photochemical aerosol formation from aromatic hydrocarbons in the presence of NO_x. Atmos. Environ. Part A 24: 1433-1441.

Javitz, H. S.; Watson, J. G.; Guertin, J. P.; Mueller, P. K. (1988) Results of a receptor modeling feasibility study. JAPCA 38: 661-667.

Johnson, J. H. (1988) Automotive emissions. In: Watson, A. Y.; Bates, R. R.; Kennedy, D., eds. Air pollution, the automobile, and public health. Washington, D.C.: National Academy Press; pp. 39-76.

Johnson, B.; Cooke, R. C. (1979) Bubble populations and spectra in coastal waters: a photographic approach. J. Geophys. Res. C: Oceans Atmos. 84: 3763-3766.

Kao, A. S.; Friedlander, S. K. (1995) Frequency distributions of PM_{10} chemical components and their sources. Environ. Sci. Technol. 29: 19-28.

Khalil, M. A. K.; Rasmussen, R. A. (1992) Forest hydrocarbon emissions: relationships between fluxes and ambient concentrations. J. Air Waste Manage. Assoc. 42: 810-813.

Kim, B. M.; Zeldin, M. D.; Liu, C. S. (1992) Source apportionment study for state implementation plan development in the Coachella Valley. In: Chow, J. C.; Ono, D. M., eds. PM10 standards and nontraditional particulate source

controls, an A&WMA/EPA international specialty conference, v. II; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 979-991. (A&WMA transactions series no. 22).

Kleinman, M. T.; Pasternack, B. S.; Eisenbud, M.; Kneip, T. J. (1980) Identifying and estimating the relative importance of sources of airborne particulates. Environ. Sci. Technol. 14: 62-65.

Koutrakis, P.; Spengler, J. D. (1987) Source apportionment of ambient particles in Steubenville, OH using specific rotation factor analysis. Atmos. Environ. 21: 1511-1519.

Lang, J. M.; Snow, L.; Carlson, R.; Black, F.; Zweidinger, R.; Tejada, S. (1982) Characterization of particulate emissions from in-use gasoline-fueled motor vehicles. Warrendale, PA: Society of Automotive Engineers; SAE technical paper no. 811186.

Lewis, C. W.; Stevens, R. K. (1987) Hybrid receptor models. In: Johnson, R. W.; Gordon, G. E.; Calkins, W.; Elzerman, A. Z., eds. The chemistry of acid rain: sources and atmospheric processes; developed from a symposium sponsored by the Divisions of Petroleum Chemistry, Inc., Nuclear Chemistry and Technology, Environmental Chemistry, and Fuel Chemistry at the 191st meeting of the American Chemical Society; April 1986; New York, NY. Washington, DC: American Chemical Society; pp. 58-65. (ACS symposium series: 349).

Lewis, C. W.; Baumgardner, R. E.; Stevens, R. K.; Claxton, L. D.; Lewtas, J. (1988) Contribution of woodsmoke and motor vehicle emissions to ambient aerosol mutagenicity. Environ. Sci. Technol. 22: 968-971.

Liousse, C.; Penner, J. E.; Chuang, C.; Walton, J. J.; Eddleman, H.; Cachier, H. (1996) A global three-dimensional model study of carbonaceous aerosols. J. Geophys. Res. [Atmos.] 101: in press.

Lioy, P. J.; Mallon, R. P.; Lippmann, M.; Kneip, T. J.; Samson, P. J. (1982) Factors affecting the variability of summertime sulfate in a rural area using principal component analysis. J. Air Pollut. Control Assoc. 32: 1043-1047.

Lowenthal, D. H.; Zielinska, B.; Chow, J. C.; Watson, J. G.; Gautam, M.; Ferguson, D. H.; Neuroth, G. R.; Stevens, K. D. (1994) Characterization of heavy-duty diesel vehicle emissions. Atmos. Environ. 28: 731-743.

Macias, E. S.; Hopke, P. K., eds. (1981) Atmospheric aerosol: source/air quality relationships; based on a symposium jointly sponsored by the Divisions of Nuclear Chemistry and Technology at the 180th national meeting of the American Chemical Society; August 1980; Las Vegas, NV. Washington, DC: American Chemical Society. (Comstock, M. J., ed. ACS symposium series: 167).

Magliano, K. L. (1988) Level 1 PM_{10} assessment in a California air basin. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 508-517. (APCA transactions series TR-13).

Marticorena, B.; Bergametti, G. (1995) Modeling the atmospheric dust cycle: I. design of a soil-derived dust emission scheme. J. Geophys. Res. [Atmos.] 100: 16,415-16,430.

Mason, B. (1966) Principles of geochemistry. 3rd ed. New York, NY: John Wiley & Sons, Inc.

Matthews, E. (1994) Nitrogenous fertilizers: global distribution of consumption and associated emissions of nitrous oxide and ammonia. Global Biogeochem. Cycles 8: 411-439.

Matthias-Maser, S.; Jaenicke, R. (1994) Examination of atmospheric bioaerosol particles with radii > 0.2 μm. J. Aerosol Sci. 25: 1605-1613.

Mazurek, M. A.; Cofer, W. R., III; Levine, J. S. (1991) Carbonaceous aerosols from prescribed burning of a boreal forest ecosystem. In: Levine, J. S., ed. Global biomass burning: atmospheric, climatic, and biospheric implications. Cambridge, MA: MIT Press; pp. 258-263.

Mylonas, D. T.; Allen, D. T.; Ehrman, S. H.; Pratsinis, S. E. (1991) The sources and size distributions of organonitrates in Los Angeles aerosol. Atmos. Environ. Part A 25: 2855-2861.

NEA. (1990a) Enhancement of the south coast air basin source profile library for chemical mass balance receptor model applications: volume I, final report. Beaverton, OR: NEA.

NEA. (1990b) Enhancement of the south coast air basin source profile library for chemical mass balance receptor model applications: volume II, source profile library supplement. Beverton, OR: NEA.

NEA. (1990c) Enhancement of the south coast air basin source profile library for chemical mass balance receptor model applications: volume III, appendices. Beverton, OR: NEA.

National Research Council. (1982) Diesel cars: benefits, risks and public policy: final report of the Diesel Impacts Study Committee. Washington, DC: National Academy Press.

Nriagu, J. O. (1989) A global assessment of natural sources of atmospheric trace metals. Nature (London) 338: 47-49.

Nriagu, J. O.; Pacyna, J. M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature (London) 333: 134-139.

O'Connor, B. H.; Kerrigan, G. C.; Hinchliffe, P. (1977) The loss of Br from thin-film samples during X-ray fluorescence analysis. X-Ray Spectrom. 6: 83-85.

Olmez, I.; Sheffield, A. E.; Gordon, G. E.; Houck, J. E.; Pritchett, L. C.; Cooper, J. A.; Dzubay, T. G.; Bennett, R. L. (1988) Compositions of particles from selected sources in Philadelphia for receptor modeling applications. JAPCA 38: 1392-1402.

Ott, S.-T.; Ott, A.; Martin, D. W.; Young, J. A. (1991) Analysis of a trans-Atlantic saharan dust outbreak based on satellite and GATE data. Mon. Weather Rev. 119: 1832-1850.

Pace, T. G., ed. (1986) Receptor methods for source apportionment: real world issues and applications, an APCA international specialty conference; March 1985; Williamsburg, VA. Pittsburgh, PA: Air Pollution Control Association. (APCA transactions no. TR-5).

Pandis, S. N.; Paulson, S. E.; Seinfeld, J. H.; Flagan, R. C. (1991) Aerosol formation in the photooxidation of isoprene and β-pinene. Atmos. Environ. Part A 25: 997-1008.

Pandis, S. N.; Harley, R. A.; Cass, G. R.; Seinfeld, J. H. (1992) Secondary organic aerosol formation and transport. Atmos. Environ. Part A 26: 2269-2282.

Peterson, J. T. (1970) Distribution of sulfur dioxide over metropolitan St. Louis, as described by empirical eigenvectors, and its relation to meteorological parameters. Atmos. Environ. 4: 501-518.

Pickle, T.; Allen, D. T.; Pratsinis, S. E. (1990) The sources and size distributions of aliphatic and carbonyl carbon in Los Angeles aerosol. Atmos. Environ. Part A 24: 2221-2228.

Pierson, W. R.; Brachaczek, W. W. (1974) Airborne particulate debris from rubber tires. Presented at: Joint meeting of the American Chemical Society, Rubber Division, and the Chemical Institute of Canada, Macromolecular Science Division; May; Toronto, Ontario, Canada. Rubber Chem. Technol. 47: 1275-1299.

Pierson, W. R.; Brachaczek, W. W. (1976) Particulate matter associated with vehicles on the road. Presented at: SAE automotive engineering congress and exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers; SAE technical paper no. 760039.

Pierson, W. R.; Brachaczek, W. W. (1983) Particulate matter associated with vehicles on the road. II. Aerosol Sci. Technol. 2: 1-40.

Pierson, W. R.; Gertler, A. W.; Bradow, R. L. (1990) Comparison of the SCAQS tunnel study with other on-road vehicle emission data. J. Air Waste Manage. Assoc. 40: 1495-1504.

Pinto, J. P.; Pleasant, M.; Kellogg, R.; Torok, Sz.; Stiles, D.; Willis, R. D.; Koutrakis, P.; Allen, G. A. (1995) Chemical characterization of the ambient aerosol in Philadelphia. Presented at: Particulate matter: health and regulatory issues: an A&WMA international specialty conference; April; Pittsburgh, PA. Pittsburgh, PA: Air & Waste Management Association; submitted abstract.

Placet, M.; Battye, R. E.; Fehsenfeld, F. C.; Bassett, G. W. (1991) Emissions involved in acidic deposition processes. In: Irving, P. M., ed. Acidic depostion: state of science and technology, volume I: emissions, atmospheric processes, and deposition. Washington, DC: The U.S. National Acid Precipitation Assessment Program. (State of science and technology report no. 1).

Prospero, J. M. (1995) The atmospheric transport of particles to the ocean. In: Ittekkot, V.; Honjo, S.; Depetris, P. J., eds. SCOPE report: particle flux in the ocean. New York, NY: John Wiley & Sons, Ltd.; in press.

Prospero, J. M.; Nees, R. T.; Uematsu, M. (1987) Deposition rate of particulate and dissolved aluminum derived from Saharan dust in precipitation at Miami, Florida. J. Geophys. Res. [Atmos.] 92: 14,723-14,731.

Prospero, J. M.; Savoie, D. L.; Arimoto, R.; Huang, F. (1993) Long-term trends in African mineral dust concentrations over the western North Atlantic: relationship to North African rainfall. EOS Trans. Am. Geophys. Union 74: 146.

Radke, L. F.; Hegg, D. A.; Hobbs, P. V.; Nance, J. D.; Lyons, J. H.; Laursen, K. K.; Weiss, R. E.; Riggan, P. J.; Ward, D. E. (1991) Particulate and trace gas emissions from large biomass fires in North America. In: Levine, J. S., ed. Global biomass burning: atmospheric, climatic, and biospheric implications. Cambridge, MA: MIT Press; pp. 209-224.

Radwan, C. (1995) Particulate emissions trends predicted in the PART5 model. In: Particulate matter: health and regulatory issues: proceedings of an international specialty conference; April; Pittsburgh, PA. Pittsburgh, PA: Air & Waste Management Association; pp. 599-607. (A&WMA publication VIP-49).

Rasmussen, R. A.; Went, F. W. (1965) Volatile organic material of plant origin in the atmosphere. Proc. Natl. Acad. Sci. U. S. A. 53: 215-220.

Reeser, W. K.; Zimmer, R. A.; Cummins, P.; Briggs, K. R. (1992) An episodic PM_{10} emissions inventory for Denver, Colorado. In: Chow, J. C.; Ono, D. M., eds. PM_{10} standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. I; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 131-145. (A&WMA transactions series no. 22).

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. (1991) Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environ. Sci. Technol. 25: 1112-1125.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. (1993a) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27: 636-651.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. (1993b) Sources of fine organic aerosol. 5. Natural gas home appliances. Environ. Sci. Technol. 27: 2736-2744.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. (1993c) Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. Environ. Sci. Technol. 27: 2700-2711.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. (1993d) Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. Environ. Sci. Technol. 27: 1892-1904.

Rogge, W. F.; Mazurek, M. A.; Hildemann, L. M.; Cass, G. R.; Simoneit, B. R. T. (1993e) Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. Atmos. Environ. Part A 27: 1309-1330.

Ryan, W. M.; Badgett-West, C. R.; Holtz, D. R.; Peters, T. A.; Cooper, J. A.; Ono, D. (1988) Reconciliation of receptor and dispersion modeling impacts of PM_{10} in Hayden, Arizona. In: Mathai, C. V.; Stonefield, D. H., eds. PM-10: implementation of standards, an APCA/EPA international specialty conference; February; San Francisco, CA. Pittsburgh, PA: Air Pollution Control Association; pp. 419-429. (APCA transactions series TR-13).

Savoie, D. L.; Prospero, J. M. (1982) Particle size distribution of nitrate and sulfate in the marine atmosphere. Geophys. Res. Lett. 9: 1207-1210.

Shao, Y.; Raupach, M. R.; Findlater, P. A. (1993) Effect of saltation bombardment on the entrainment of dust by wind. J. Geophys. Res. [Atmos.] 98: 12,719-12,726.

Skidmore, L. W.; Chow, J. C.; Tucker, T. T. (1992) PM_{10} air quality assessment for the Jefferson County, Ohio air quality control region. In: Chow, J. C.; Ono, D. M., eds. PM_{10} standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. II; January; Scottsdale, AZ. Pittsburgh, PA: Air and Waste Management Association; pp. 1016-1031. (A&WMA transactions series no. 22).

Snow, J. T.; McClelland, T. M. (1990) Dust devils at White Sands Missile Range, New Mexico: 1. temporal and spatial distributions. J. Geophys. Res. [Atmos.] 95: 13,707-13,721.

South Coast Air Quality Management District. (1994) State implementation plan for PM10 in the Coechella Valley: 1994 "BACM" revision. Diamond Bar, CA: South Coast Air Quality Management District.

Spendlove, J. C. (1974) Industrial, agricultural, and municipal microbial aerosol problems. In: Current problems in aerobiology: proceedings of the thirtieth general meeting of the Society for Industrial Microbiology; August 1973; Evanston, IL. Dev. Ind. Microbiol. 15: 20-27.

Stevens, R. K.; Pace, T. G. (1984) Overview of the mathematical and empirical receptor models workshop (Quail Roost II). Atmos. Environ. 18: 1499-1506.

Stevenson, H. J. R.; Sanderson, D. E.; Altshuller, A. P. (1965) Formation of photochemical aerosols. Int. J. Air Water Pollut. 9: 367-375.

Susott, R. A.; Ward, D. E.; Babbitt, R. E.; Latham, D. J. (1991) The measurement of trace emissions and combustion characteristics for a mass fire. In: Levine, J. S., ed. Global biomass burning: atmospheric, climatic, and biospheric implications. Cambridge, MA: MIT Press; pp, 245-257.

Svasek, J. N.; Terwindt, J. H. J. (1974) Measurements of sand transport by wind on a natural beach. Sedimentology 21: 311-322.

Szkarlat, A. C.; Japar, S. M. (1983) Optical and chemical properties of particle emissions from on-road vehicles. J. Air Pollut. Control Assoc. 33: 592-597.

Thanukos, L. C.; Miller, T.; Mathai, C. V.; Reinholt, D.; Bennett, J. (1992) Intercomparison of PM10 samplers and source apportionment of ambient PM10 concentrations at Rillito, Arizona. In: Chow, J. C.; Ono, D. M., eds. PM_{10} standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. I; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 244-261. (A&WMA transactions series no. 22).

Truex, T. J.; Pierson, W. R.; McKee, D. E. (1980) Sulfate in diesel exhaust. Environ. Sci. Technol. 14: 1118-1121.

Turekian, K. K. (1971) Elements, geochemical distribution of. In: Encyclopedia of science and technlogy, v. 4. New York, NY: McGraw-Hill Book Company; pp. 627-630.

Turpin, B. J.; Huntzicker, J. J. (1991) Secondary formation of organic aerosol in the Los Angeles basin: a descriptive analysis of organic and elemental carbon concentrations. Atmos. Environ. Part A 25: 207-215.

Turpin, B. J.; Huntzicker, J. J.; Larson, S. M.; Cass, G. R. (1991) Los Angeles summer midday particulate carbon: primary and secondary aerosol. Environ. Sci. Technol. 25: 1788-1793.

U.S. Environmental Protection Agency. (1989) Procedures for estimating and applying rule effectiveness in post-1987 base year emission inventories for ozone and carbon monoxide state implementation plans. Research Triangle Park, NC: Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency. (1993) Motor vehicle-related air toxics study. Ann Arbor, MI: Office of Mobile Sources; EPA report no. EPA/420/R-93/005. Available from: NTIS, Springfield, VA; PB93-182590/XAB.

U.S. Environmental Protection Agency. (1994) National air quality and emissions trends report, 1993. Research Triangle Park, NC: Office of Air Quality Planning and Standards; EPA report no. EPA 454/R-94-026.

U.S. Environmental Protection Agency. (1995a) Compilation of air pollutant emission factors, volume I: stationary point and area sources. 5th ed. Research Triangle Park, NC: Office of Air Quality Planning and Standards; report no. AP-42.

U.S. Environmental Protection Agency. (1995b) National air pollutant emission trends, 1900 - 1994. Research Triangle Park, NC: Office of Air Quality Planning and Standards; report no. EPA-454/R-95-011.

Van Espen, P. (1984) A program for the processing of analytical data (DPP). Anal. Chim. Acta 165: 31-49.

Vermette, S. J.; Williams, A. L.; Landsberger, S. (1992) PM_{10} source apportionment using local surface dust profiles: examples from Chicago. In: Chow, J. C.; Ono, D. M., eds. PM_{10} standards and nontraditional particulate source controls, an A&WMA/EPA international specialty conference, v. I; January; Scottsdale, AZ. Pittsburgh, PA: Air & Waste Management Association; pp. 262-278. (A&WMA transactions series no. 22).

Vinogradov, A. P. (1959) The geochemistry of rare and dispersed chemical elements in soils. 2nd ed. New York, NY: Consultants Bureau, Inc.

Walker, B. L.; Cooper, C. D. (1992) Air pollution emission factors for medical waste incinerators. J. Air Waste Manage. Assoc. 42: 784-791.

Warneck, P. (1988) Chemistry of the natural atmosphere. New York, NY: Academic Press, Inc.

Watson, J. G.; Chow, J. C. (1994) Clear sky visibility as a challenge for society. Annu. Rev. Energy Environ. 19: 241-266.

Watson, J. G.; Henry, R. C.; Cooper, J. A.; Macias, E. S. (1981) The state of the art of receptor models relating ambient suspended particulate matter to sources. In: Macias, E. S.; Hopke, P. K., eds. Atmospheric aerosol: source/air quality relationships; based on a symposium jointly sponsored by the Divisions of Nuclear Chemistry and Technology and Environmental Chemistry at the 180th national meeting of the American Chemical Society; August 1980; Las Vegas, NV. Washington, DC: American Chemical Society; pp. 89-106. (Comstock, M. J., ed. ACS symposium series: 167).

Watson, J. G.; Chow, J. C.; Mathai, C. V. (1989) Receptor models in air resources management: a summary of the APCA international specialty conference. JAPCA 39: 419-426.

Watson, J. G.; Chow, J. C.; Pritchett, L. C.; Houck, J. A.; Burns, S.; Ragazzi, R. A. (1990a) Composite source profiles for particulate motor vehicle exhaust source apportionment in Denver, CO. In: Mathai, C. V., ed. Visibility and fine particles: an A&WMA/EPA international specialty conference; October 1989; Estes Park, CO. Pittsburgh, PA: Air & Waste Management Association; pp. 422-436. (A&WMA transactions series no. TR-17).

Watson, J. G.; Chow, J. C.; Pritchett, L. C.; Houck, J. A.; Ragazzi, R. A.; Burns, S. (1990b) Chemical source profiles for particulate motor vehicle exhaust under cold and high altitude operating conditions. Sci. Total Environ. 93: 183-190.

Watson, J. G.; Chow, J. C.; Pace, T. G. (1991) Chemical mass balance. In: Hopke, P. K., ed. Data handling in science and technology: v. 7, receptor modeling for air quality management. New York, NY: Elsevier Press; pp. 83-116.

Watson, J. G.; Chow, J. C.; Lowenthal, L. C.; Pritchett, C. A.; Frazier, C. A.; Neuroth, G. R.; Robbins, R. (1994a) Differences in the carbon compostion of source profiles for diesel- and gasoline-powered vehicles. Atmos. Environ. 28: 2493-2505.

Watson, J. G.; Chow, J. C.; Blumenthal, D. L.; Lurmann, F. W.; Hackney, R. J.; Magliano, K. L.; Pederson, J. R.; Neff, W. D.; Roth, P. M.; Solomon, P. A.; Thuillier, R. H.; Ziman, S. D. (1994b) Planning for data analysis. In: Solomon, P. A.; Silver, T. A., eds. Planning and managing regional air quality modeling and measurement studies: a perspective through the San Joaquin Valley air quality study and AUSPEX. Boca Raton, FL: Lewis Publishers; pp. 335-349.

Went, F. W. (1960) Organic matter in the atmosphere, and its possible relation to petroleum formation. Proc. Natl. Acad. Sci. U. S. A. 46: 212-221.

Wilson, T. R. S. (1975) Salinity and major elements of sea water. In: Riley, J. P.; Skirrow, G., eds. Chemical oceanography. 2nd ed. London, United Kingdom: Academic Press; pp. 365-413.

Wilson, W. E.; Schwartz, W. E.; Kinzer, G. W. (1972) Haze formation—its nature and origin. New York, NY: Coordinating Research Council; report no. CRC-APRAC-CAPA-6-68-3. Available from: NTIS, Springfield, VA; PB-212609.

Wolff, G. T.; Korsog, P. E. (1985) Estimates of the contributions of sources to inhalable particulate concentrations in Detroit. Atmos. Environ. 19: 1399-1409.

Wolff, G. T.; Countess, R. J.; Groblicki, P. J.; Ferman, M. A.; Cadle, S. H.; Muhlbaier, J. L. (1981) Visibility-reducing species in the Denver "brown cloud"—II. sources and temporal patterns. Atmos. Environ. 15: 2485-2502.

Wolff, G. T.; Korsog, P. E.; Kelly, N. A.; Ferman, M. A. (1985a) Relationships between fine particulate species, gaseous pollutants and meteorological parameters in Detroit. Atmos. Environ. 19: 1341-1349.

Wolff, G. T.; Korsog, P. E.; Stroup, D. P.; Ruthkosky, M. S.; Morrissey, M. L. (1985b) The influence of local and regional sources on the concentration of inhalable particulate matter in southeastern Michigan. Atmos. Environ. 19: 305-313.

Wu, J. (1979) Sea spray in the atmospheric surface layer: review and analysis of laboratory and oceanic results. J. Geophys. Res. [Atmos.] 84: 1683-1704.

Xie, Y.; Hopke, P. K.; Casuccio, G.; Henderson, B. (1994a) Use of multiple fractal dimensions to quantify airborne particle shape. Aerosol Sci. Technol. 20: 161-168.

Xie, Y.; Hopke, P. K.; Casuccio, G.; Henderson, B. (1994b) Use of chain code histogram method to quantify airborne particle shapes. Aerosol Sci. Technol. 21: 210-218.

Zeng, Y.; Hopke, P. K. (1989) Three-mode factor analysis: a new multivariate method for analyzing spatial and temporal composition variation. In: Watson, J. G., ed. Receptor models in air resources management: an international specialty conference; February 1988; San Francisco, CA. Pittsburgh, PA: Air & Waste Management Association; pp. 173-189. (APCA transactions series: no. 14).

Zhang, S.-H.; Shaw, M.; Seinfeld, J. H.; Flagan, R. C. (1992) Photochemical aerosol formation from α-pinene and β-pinene. J. Geophys. Res. [Atmos.] 97: 20,717-20,729.